



The Seventh International Symposium on
Polymer Electrolytes, Noosa, AUSTRALIA
6th - 11th August 2000

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1. Conference Proceedings from "The Seventh International Symposium on Polymer Electrolytes", held 6-11 Aug 00, in Noosa, Australia, is attached as a DTIC submittal.
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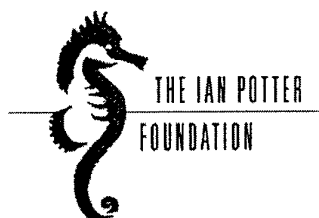
Attachments:

1. AF Form 298/Documentation Page (CSP-98-29)
2. DTIC Form 50/DTIC Accession Notice
3. Conference Proceedings of "The Seventh International Symposium on Polymer Electrolytes"

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Steve Pas

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WELCOMING REMARKS

Welcome to the 7th International Symposium on Polymer Electrolytes (ISPE7) and to the sunny shores of the Sunshine Coast in Queensland, Australia. The field of polymer electrolytes is still an important area of research within the international community, as is evidenced by the strong international flavour of the 100 or so delegates who have come from North America, Japan, Korea, UK, Sweden, Brazil, Germany, Taiwan, Italy, New Zealand, Poland, Scotland, Portugal, the Netherlands, Israel, the Ukraine, Colombia and of course, the host country, Australia. With the continuing push to clean up our environment and to produce alternative energy sources, we still find a strong emphasis on polymer electrolyte research for battery applications, with an increasing number of researchers exploring alternative proton conductors for polymer membrane fuel cells. You will hear 12 invited talks, and view more than 100 oral and poster presentations in the areas of new materials, gel electrolytes, nanocomposite materials, modelling, spectroscopy, proton conductors and applications. The social programme has been chosen to give you an introduction to Australian traditions with an Aussie BBQ planned for Tuesday night, a port tasting at the poster session on Wednesday night and an Australian Theme dinner on Thursday evening. We hope you enjoy the technical content of the conference, make new friends and collaborators and most of all, have fun at ISPE7.

Maria Forsyth
Doug MacFarlane
Astrid Nordmann

ISPE7

Sunday 6 th August	Monday 7 th August	Tuesday 8 th August	Wednesday 9 th August	Thursday 10 th August	Friday 11 th August
	8.00am-9.00am Registration	8.30am-9.00am Registration	8.30am – 9.00am Registration		9.00am-11.00am Impedance Spectroscopy Workshop Part I
	9.00am-10.30am Opening Ceremony & Plenary Session I	9.00am – 10.40am Gels I	9.00am-10.40am Applications I	8.45am-10.40am Theory & Spectroscopy I	
	10.30am-11.00am <i>Tea/Coffee</i>	10.40am-11.10am <i>Tea/Coffee</i>	10.40am-11.10am <i>Tea/Coffee</i>	10.40am-11.10am <i>Tea/Coffee</i>	11.00am-11.30am <i>Tea/Coffee</i>
	11.00am-1.00pm Plenary Session II	11.10am-12.50pm Gels II	11.10-12.50pm Applications II	11.10am-12.50pm Theory & Spectroscopy II	11.30-1.00pm Impedance Spectroscopy Workshop Part II
	1.00pm-2.00pm <i>Lunch</i>	12.50pm-2.00pm <i>Lunch</i>	12.50pm-2.00pm <i>Lunch</i>	12.50pm-2.00pm <i>Lunch</i>	1.00pm-2.00pm <i>Lunch</i>
4.00pm-6.00pm Registration	2.00pm-4.00pm <i>Free time</i>	2.00pm-4.00pm <i>Free time</i>	2.00pm-6.30pm Excursion	2.00pm-3.40pm <i>Free time</i>	End of Conference
	4.00pm-5.20pm Plenary Session III	4.00pm-6.20pm New Systems		3.40pm-6.00pm Composites & Proton Conductors	
6.00pm-7.30pm Welcoming Reception	5.20pm-6.45pm Poster Session I	6.45pm-8.00 pm Aussie BBQ	8.00pm-9.30pm Port & Poster Session II	7.30pm-11.00pm Conference Dinner	

Sunday, 6th August

REGISTRATION

Sheraton Ballroom Lobby

4:00pm - 6:00pm

WELCOMING RECEPTION

Rendezvous Lounge

6:00pm - 7:30pm

Monday, 7th August

OPENING CEREMONY AND PLENARY SESSION I

Sheraton Ballroom

9:00am - 10:30am

Chaired by Prof. Doug MacFarlane & Prof. Steve Greenbaum

Assistants: Adam Best and Kate Nairn

9:00am Welcoming Remarks

M. Forsyth

9:10am Strategy, structure and serendipity in low-dimensional polymer electrolytes

P.V. Wright, Y. Zheng, F.S. Chia and G. Ungar

9:50am Molten salt type polymer electrolytes

H. Ohno

Morning refreshments

Sheraton Ballroom Lobby

10:30am - 11:00am

PLENARY SESSION II

Sheraton Ballroom

11:00am - 1:00pm

Chaired by Prof. Doug MacFarlane & Prof. Steve Greenbaum

Assistants: Adam Best and Kate Nairn

11:00am Ion transport in glassy polymer electrolytes

M. D. Ingram and C.T. Imrie

11:40am Mechanisms of transport in proton-conducting membranes for fuel cell applications

T.A. Zawodzinski Jr., S.J. Paddison, R. Paul and L.R. Pratt

12:20pm Computer simulation studies of structure and relaxation of polymer electrolytes

S. W. de Leeuw and A. van Zon

Lunch

Rendezvous Lounge

1:00pm - 2:00pm

PLENARY SESSION III

Sheraton Ballroom

4:00pm - 5:20pm

Chaired by Prof. Simon de Leeuw & Prof. Michel Armand

Assistants: Hayley Every and Scott Thompson

4:00pm Non-aqueous proton conducting gel electrolytes: basic research and applications

W. Wieczorek, G. Zukowska and R. Borkowska

4:40pm Polymer in plastic crystal electrolytes

D.R. MacFarlane and M. Forsyth

POSTER SESSION I

Sheraton Ballroom Lobby

5:20pm - 6:45pm

PA1 - Nano-composite electrolytes for use in novel lithium battery applications

I.J.C.M.E. Wolterink, M.J.G. Jak, A.S. Best, M. Forsyth and D.R. MacFarlane

PA2 - Amorphous nanocomposite electrolytes: issues affecting conductivity

A.S. Best, J. Adebahr, D.R. MacFarlane and M. Forsyth

PA3 - Preparation and electrochemical characteristics of the plasticized polymer electrolyte based on P(VdF-co-HFP)/PVAc blend

N-S. Choi, Y-G. Lee and J-K. Park

PA4 - Zeolitic inorganic-organic polymer electrolytes: synthesis, characterization and ionic conductivity of a material based on oligo(ethylene glycol)600, $\text{Sn}(\text{CH}_3)_2\text{Cl}_2$ and $\text{K}_4\text{Fe}(\text{CN})_6$

V. Di Noto, M. Fauri, S. Lavina and S. Biscazzo

PA5 - Poly-vinyl-pyrrolidone in lithium doped plastic salt electrolytes

S. Pas, J. Golding, D.R. MacFarlane and M. Forsyth

PA6 - Influence of the degree of sulfonation on the water uptake and proton conductivity for acryl amide copolymers

L. Karlsson, P. Jannasch and B. Wesslen

PA7- XPS study of the lithium surface after contact with lithium-salt doped polymer electrolytes

I. Ismail, A. Noda, A. Nishimoto and M. Watanabe

PA8 - Electron transfer reaction of poly(ethylene oxide)-modified azurin in poly (ethylene oxide) oligomers and organic solvents

N. Nakamura, Y. Nakamura, N.Y. Kawahara, H. Ohno, Deligeer and S. Suzuki

PA9 - Polypyrrole-based biosensor for the determination of cholesterol

G. Govender, S.B. Adeloju and A.N. Moline

PA10 - Fabrication of a polypyrrole-dextran-sulfite oxidase biosensor

A. Ohanessian, S.B. Adeloju and A.N. Moline

PA11 - Control of ionic conductivity using boron compounds

T. Hirakimoto, M. Nishiura and M. Watanabe

PA12 - NMR and ion conductivity studies of a ethyleneoxide-propyleneoxide precursor monomer doped by $\text{LiN}(\text{SO}_2\text{CF}_3)_2$

K. Sugimoto, Y. Aihara and K. Hayamizu

PA13 - Microporous polymer electrolyte membranes

A. Munch, P. Jannasch and B. Wesslén

- PA14** - Effect of high pressure on the electrical conductivity of ion conducting polymers
J.J. Fontanella, J.T. Bendler, M.F. Shlesinger and M.C. Wintersgill
- PA15** - Complex impedance and NMR studies of S-SEBS block polymer proton-conducting membranes
C.A. Edmondson, J.J. Fontanella, S.H. Chung, S.G. Greenbaum and G. E. Wnek
- PA16** - Study of electrochemical supercapacitors using polyurethane electrolytes/carbon black composites
C.A. Furtado, P.P. de Souza, G. G. Silva, J.M. Pernaut and T. Matencio
- PA17** - Measurement of electrochemical stability of gel electrolytes for lithium batteries
K. Edstroem, T. Eriksson, L. Fransson, P. Gavelin, P. Georén, T. Gustafsson, P. Jannasch, G. Lindbergh, J. O. Thomas and B. Wesslén
- PA18** - Poly(propylene oxide)/sulfonamide salt hybrids as new ion conductive polymers
T. Mizumo, Y. Tominaga and H. Ohno
- PA19** - Preparation and characterization of a novel lithium salt based polymer electrolyte
M.M. Silva, S. C. Barros, M. J. Smith and J. R. MacCallum
- PA20** - Binding isotherms calculated for interaction of Cu^{2+} and Ca^{2+} ions with DNA on its compactisation in terms of statistical sum of macromolecule
E.V. Hackl, V.L. Galkin and Yu. P. Blagoi
- PA21** - Optical transparent ion conducting modified polymethylmethacrylate polymer
G.M. Mokrousov and N.A. Gavrilenko
- PA22** - SANS study on interaction of micellar aggregates and microemulsions of polyelectrolyte copolymers
Z.J. Li, J.S. Huang and M.Y. Lin
- PA23** - PVDF-based porous polymer electrolytes
A. Magistris, P. Mustarelli, E. Quartarone, P. Piaggio and A. Bottino
- PA24** - Preparation of poly (propylene carbonate) based gelled polymer electrolytes for lithium polymer battery
Y.M. Kim, D. Y. Seung and M.D. Cho
- PA25** - A density functional study of the bis[(trifluoromethane)sulfonyl]amide (TFSA⁻) based salts using a TFSA⁻Li⁺ model
K. Baranyai, D. R. MacFarlane, P. D. Godfrey and M. Forsyth
- PA26** - Current R&D at the Angstrom Advanced Battery Centre
S. Abbrent, A.M. Andersson, A. Bishop, H. Bjork, K. Estrom, T. Eriksson, P. Eyob, L. Fransson, T. Gustafsson, M. Herstedt, J. Howling, S. Nordlinder, J. Lindgren, J. Tegenfeldt and J.O. Thomas
- PA27** - Testing polymer membranes for an electrowinning process
P.A. Adcock
- PA28** - Electrolytes based on aggregating comblike poly(ethylene oxide-co-propylene oxide)
P. Jannasch
- PA29** - NMR and ionic conductivity study of non-aqueous proton gel electrolytes based on poly(vinylidene fluoride) and H_3PO_4
S.H. Chung, Y. Wang, S.G. Greenbaum, G. Zukowska and W. Wieczorek
- PA30** - Platinum electrodeposition for polymer electrolyte membrane fuel cells
S.D. Thompson, L.R. Jordan, A.K. Shukla, M. Forsyth and B.C. Muddle
- PA31** - NMR, DSC and conductivity study of HEC/polyether based polymer electrolyte
C. E. Tambelli, A.M. Regiani, A. Pawlicka, A.A.S. Curvelo, J.P. Donoso, A. Gandini and J.-F. LeNest

Tuesday, 8th August

GEL ELECTROLYTES I

Sheraton Ballroom

9:00am - 10:40am

Chaired by Dr. Denis Fauteux & Prof. Bruno Scrosati

Assistants: Jewel Huang and Stewart Forsyth

- 9:00am Gel electrolytes - the relationship between charge carrier mobility and structure of the polymer
A. Reiche, A. Weinkauff, B. Sandner, G. Dlubek, C. Papadakis, P. Busch, G. Fleischer, W. Meyer
- 9:20am Amphiphilic polymer gel electrolytes: Influence of the hydrophobic-hydrophilic balance on the ion
R. Ljungbaeck, P. Gavelin, P. Jannasch and B. Wesslen
- 9:40am Diffusion of solvent/salt and segmental relaxation in polymer gel electrolytes
C. Svanberg, R. Bergman, L. Borjesson and P. Jacobsson
- 10:00am Structural properties, thermal stability and electrochemical characteristics of gel polymeric electrolytes based on chlorinated polyvinylchloride
E.M. Shembel, O.V. Chervakov, A.G. Ribalka, L.I. Neduzhko, D. Golodnitsky, D.T. Meshri and D.E. Reisner
- 10:20am Solvent containing polyacrylic network as a solid electrolyte
T.I. Isaak and G.M. Morousov

Morning refreshments

Sheraton Ballroom Lobby

10:40am - 11:10am

GEL ELECTROLYTES II

Sheraton Ballroom

11:10am - 12:50pm

Chaired by Prof. Josh Thomas

Assistants: Jewel Huang and Stewart Forsyth

- 11:10am **Plenary:** New polymer electrolyte for plastic lithium ion battery
J-K. Park and N-S. Choi
- 11:50am Ion conductivity of novel polyelectrolyte gels for secondary lithium polymer batteries
J. Travas-Sejdic, R. Steiner, J. Desilvestro and P. Pickering
- 12:10pm Thermal stability investigations on PVDF-based novel Li⁺ conducting solid polymer electrolyte blends for Li-ion batteries
S.R.S. Prabaharan, T.Y. Tou, R.A. Adnan and M.S. Michael
- 12:30pm Ion dynamics in polyether solid polymer electrolytes using AC impedance
P. Meakin, M. Forsyth and D. R. MacFarlane

Lunch

Rendezvous Lounge

12:50pm - 2:00pm

NEW SYSTEMS

Sheraton Ballroom

4:00pm - 6:20pm

Chaired by Dr. Anita Hill & Dr. Annette Reiche

Assistants: Pavla Meakin and Steve Pas

- 4:00pm Anion-trapping polyethers and related polymers for S-in-P and P-in-S electrolytes
X. Sun and C. Austen Angell
- 4:20pm NMR and ion conductivity studies on the cross-linked poly(ethyleneoxide-propyleneoxide) block polymer doped by $\text{LiN}(\text{SO}_2\text{CF}_3)_2$
K. Hayamizu, Y. Aihara and W.S. Price
- 4:40pm Control of lithium transference number by using lithium salt of perfluorinated polyimide complexed with polyether
M. Watanabe, S. Muto and Y. Suzuki
- 5:00pm High ambient dc and ac conductivities in solvent-free low-dimensional polymer electrolyte blends with lithium salts
Y. Zheng, F. Chia, G. Ungar, T.H. Richardson and P.V. Wright
- 5:20pm Electrochemical and physiochemical properties of polymer electrolytes containing room temperature molten salts
A. Noda, T. Kaneko and M. Watanabe
- 5:40pm Structure and conductivity in polydioxolane/ LiCF_3SO_3 electrolytes
R.A. Silva, G. Goulart Silva, C.A. Furtado and M.A. Pimenta
- 6:00pm Novel polymer electrolytes with borate structures as anion receptors for lithium secondary batteries
M. Nishiura, T. Hirakimoto, M. Kono and M. Watanabe

Wednesday, 9th August

APPLICATIONS I

Sheraton Ballroom

9:00am - 10:40am

Chaired by Prof. Hiroyuki Ohno & Dr. Andrea Bishop

Assistants: Kristian Baranyai and Patrick Howlett

- 9:00am **Plenary:** Interfacial behaviour of anode additives in polymer electrolyte systems
D. Fauteux
- 9:40am New polymer lithium secondary batteries based on ORMOCER electrolytes (inorganic-organic polymers)
M. Popall, R. Buestrich, G. Semray, G. Eichinger, M. Andrei, W.O. Parker, S. Skaarup and K. West
- 10:00am Humidity sensor based on alkali salts of poly (2-acrylamido-2-methylpropane sulfonic acid)
Y. Sakai, M. Matsuguchi and N. Yonesato
- 10:20am Solid polymer electrolytes: the limiting factor in polymer actuator performance
T.W. Lewis, B. Kim, G.M. Spinks and G.G. Wallace

Morning refreshments

Sheraton Ballroom Lobby

10:40am - 11:10am

APPLICATIONS II

Sheraton Ballroom

11:10am - 12:50pm

Chaired by Prof. Roger Frech & Dr. Maria Forsyth

Assistants: Kristian Baranyai and Patrick Howlett

- 11:10am Polyether electrolytes for lithium battery applications
A.G. Bishop, J.O. Thomas and D.R. MacFarlane
- 11:30am Structural evolution and conductivity of PEO:LiBF₄-MgO composite electrolytes
B. Kumar, L.G. Scanlon, R. A. Marsh, R. Mason, R. Higgins and R. S. Baldwin
- 11:50am Electrochemistry of planar solid-state amperometric devices based on Nafion[®] and polybenzimidazole (PBI) solid polymer electrolytes
K. Wallgren and S. Sotiropoulos
- 12:10pm Discharge studies of polymer electrolyte based electrochemical cells
R. Chandrasekaran and S. Selladurai
- 12:30pm An all solid-state photoelectrochromic window with poly (ethylene oxide) (PEO) gel electrolyte
L. Su

Lunch

Rendezvous Lounge

12:50pm - 1:50pm

PORT & POSTER SESSION II

Sheraton Ballroom Lobby

8:00pm - 9:30pm

- PB1 - A proton conductor based on silicotungstic acid
J. Sun, L. Jordan, M. Forsyth and P.R. MacFarlane
- PB2 - Studies in liquid crystalline polymer electrolytes
L.J. Barlow, C.T. Imrie and M.D. Ingram
- PB3 - Novel proton conducting polymer electrolytes for electrochromic systems
Z. Florjanczyk, E. Zygadco-Monikowska, A. Wojda and W. Wieczorek
- PB4 - Proton conducting polymer gels containing heteropolyacids
G. Zukowska, R. Borkowska, K. Tkaczyk, P. Kuzma and W. Wieczorek
- PB5 - Novel "polymer in salt" type electrolytes
A. Zalewska, E. Sulek, G. Zukowska and W. Wieczorek
- PB6 - Polymer solid electrolytes with enhanced cation transport number
A. Blazejczyk and W. Wieczorek
- PB7 - A comparison of ionic conductivity, thermal behaviour and morphology in two polyethers-LiI-LiAl₅O₈ composite polymer electrolytes
R. Ribeiro, G. Goulart Silva and N.D.S. Mohallem
- PB8 - Micro-Raman study of polymer electrolytes near phase segregation compositions
R.A. Silva, G. Goulart Silva and M.A. Pimenta
- PB9 - New solid ionic conductor based on poly(ethylene oxide) and sodium acetate
J. Castillo and R.A. Vargas
- PB10 - More thermal studies on the PVA1 + H₃PO₂ + H₂O solid proton conductor gel
R.A. Vargas, V.H. Zapata, E. Matallana and M.A. Vargas
- PB11 - Ion transport properties in high molecular weight polyether comb polymers
H. Tokuda, S. Muto, A. Noda and M. Watanabe
- PB12 - Acid + organic base doped polymers for fuel cell electrolytes
L.R. Jordan, J. Sun, M. Forsyth and D.R. MacFarlane
- PB13 - Ionic conductivity and interfacial studies of thin film polymer electrolyte (PEO:LiF₆PO₄)/Li₂O.V₂O₅ electrode
R. Vasanthi, I. Ruth Mangani and S. Selladurai
- PB14 - Anomalous diffusion in imidazolium iodide salts
G. Orädd, A. Ferry, H.A. Every, M. Forsyth, D.R. MacFarlane and A.G. Bishop
- PB15 - Lithium ion conductivity in polyoxyethylene/polyethylenimine blends
R. Tanaka, M. Sakurai, H. Sekiguchi, H. Mori, T. Murayama and T. Ooyama
- PB16 - Molecular dynamics simulations of PEO-NaI polymer electrolytes
A. van Zon, S.W. de Leeuw, B. Mos and P. Verkerk
- PB17 - Synthesis of molten salt-type polymer brush and effect of brush structure on the ionic conductivity
M. Yoshizawa and H. Ohno
- PB18 - All solid-state smart window of electrodeposited WO₃ and SnO₂/MO film with polymer gel electrolyte
L. Su
- PB19 - Preparation of ion conductive DNA films
N. Takizawa and H. Ohno
- PB20 - PEO-based nanocomposite polymer electrolytes: an impedance spectroscopy study
F. Croce, L. Persi, R. Marassi and B. Scrosati

PB21 - Study on the redox reaction of poly (ethylene oxide) - derivative modified myoglobin on the electrode surface in PEO oligomers

A. Sato, T. Matsuo, N. Kawahara and H. Ohno

PB22 - Composite polyether electrolytes with Lewis acid type additives

A. Zalewska, R. Borkowska, A. Redo, J. Trebik, J. Tyminska and W. Wieczorek

PB23 - Growth and characterization of lead-sulfide deposited on glass substrates

S.M. Salim

PB24 - Local free volume and structure of polymer gel electrolytes on the basis of alternating copolymers

A. Reiche, G. Dlubek, A. Weinkauff, B. Sandner, G. Fleischer, F. Rittig and J. Kaerger

PB25 - Pyrrolidinium tetrafluoroborate ionic liquids as potential salts for polymer electrolytes

S. Forsyth, J. Golding, D.R. MacFarlane and M. Forsyth

PB26 - A NMR study of polymer gel electrolytes based on a polymer with grafted PEO-side chains

J. Adebahr, P. Gavelin, P. Jacobsson, D.R. MacFarlane and M. Forsyth

PB27 - Free volume and ionic mobility in nanocomposites of polyether electrolytes studied by positron annihilation lifetime spectroscopy (PALS) and Li-7 NMR

J. Adebahr, A.S. Best, A. Hill, P. Jacobsson, D.R. MacFarlane and M. Forsyth

PB28 - Conduction properties of lithium gel electrolytes investigated by impedance spectroscopy and pulsed-field gradient NMR with electric field

Y. Saito, H. Kataoka, H. Yamamoto, T. Sakai and S. Deki

PB29 - Effect of moisture on mobility in polyacrylonitrile-lithium triflate electrolytes

T.J. Bastow, K.M. Naim, J. Sun and M. Forsyth

PB30 - Lithium ion conduction in ceramic polymer composites

K.M. Naim, M. Forsyth and D.R. MacFarlane

Thursday, 10th August

THEORY/SPECTROSCOPY I

Sheraton Ballroom

9:00am - 10:40am

Chaired by Prof. C. Austen Angell

Assistants: Josefina Adebahr and Larry Jordan

8:45am **Plenary:** Applicability of free volume theories to mechanisms of conduction in polymer electrolytes

A. J. Hill, D.R. MacFarlane and M. Forsyth

9:25am A comparative vibrational spectroscopic study of lithium triflate and sodium triflate in linear poly(ethyleneimine)

S. York, R. Frech, A. Snow and D. Glatzhofer

9:45am Optical absorption spectra as a local structural probe of PEO

D. Brandell, M. Klintenberg, A. Aabloo and J. O. Thomas

10:05am A Rouse model for polymer electrolytes

A. van Zon and S.W. de Leeuw

10:25am Advances in FTIR spectroscopy of polymers

J. Gonis

Morning refreshments

Sheraton Ballroom Lobby

10:40am - 11:10am

THEORY/SPECTROSCOPY II

Sheraton Ballroom

11:10am - 12:50pm

Chaired by Prof. Jung-ki Park & Prof. Malcolm Ingram

Assistants: Josefina Adebahr and Larry Jordan

11:10am **Plenary:** New lithium salts on the computer: fiction or fact?

P. Johansson and P. Jacobsson

11:50am A vibrational spectroscopic study of lithium triflate in polyphosphazenes with linear oligoethyleneoxy side chains of different lengths

S. York, E.C. Kellam III, H.R. Allcock and R. Frech

12:10pm Molecular dynamics simulation of the 'plasticizing' effect of Al₂O₃ nano-particles on ion transport in the PEO-LiCl system

H. Kasemagi, M. Klintenberg, A. Aabloo and J. O. Thomas

12:30pm Diffusion in novel salts

Lunch

Rendezvous Lounge

12:50pm - 2:00pm

COMPOSITES AND PROTON CONDUCTORS

Sheraton Ballroom

3:40pm - 6:00pm

Chaired by Prof. Masayoshi Watanabe & Dr. Patrik Johansson

Assistants: Jiazeng Sun and Jim Efthimiades

3:40pm **Plenary:** Lithium and proton conducting gel-type electrolyte membranes

B. Scrosati and S. Panero

4:20pm A heteropolyacid-polymer proton conductor for application in polymer electrolyte fuel cells

L. Jordan, D.R. MacFarlane, I. Burgar and M. Forsyth

4:40pm Nano-structure of nafion: a SAXS study

H.-G. Haubold, Th. Vad, H. Jungbluth and P. Hiller

5:00pm The role of the inorganic oxide in nanocomposite polymer and gel electrolyte structure and ion transport mechanism: an NMR study

S.G. Greenbaum, S.H. Chung, Y. Wang, X. Guo, L. Persi, S. Panero, F. Croce and B. Scrosati

5:20pm Ionic conductance behaviour of polymeric composite solid electrolytes containing lithium aluminate

M. Morita, T. Fujisaki, N. Yoshimoto and M. Ishikawa

5:40pm NMR and DSC study of PEO-based composite polymer electrolytes

A.C. Bloise, C.C. Tambelli, R.W.A. Franco, C.J. Magon, J.P. Donoso, M.F. de Souza, A.V. Rosario and E.C. Pereira

Closing Remarks

6:00pm

CONFERENCE DINNER

Noosa Lakes Resort

7:00pm - 11:00pm

Friday, 11th August

WORKSHOP ON IMPEDANCE ANALYSIS: PART 1

Mapleton Room

9:30am - 10:30am

9:30am Complex impedance measurement of conductivity
P. Meakin

10:00am Impedance formalisms and fitting
K. Naim

Morning refreshments

Montville Room

10:30am - 11:00am

WORKSHOP ON IMPEDANCE ANALYSIS: PART 2

Mapleton Room

11:00am - 12:30pm

11:00am The modulus controversy and dispersive conductivity phenomena
M. Ingram

11:40am Interpretation of impedance data for dispersed systems
W. Wiecek

Sandwich lunch for participants

Montville Room

12:30pm - 1:30pm

ABSTRACTS

OPENING CEREMONY AND PLENARY SESSION I

Chairpersons:

**Prof. Doug MacFarlane
Monash University, Australia
&**

**Prof. Steve Greenbaum
Hunter College of CUNY, USA**

MOLTEN SALT TYPE POLYMER ELECTROLYTES

Hiroyuki Ohno

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Tokyo University of Agriculture & Technology,
Koganei, Tokyo 184-8588, Japan*

Combination of N-substituted imidazolium cations and organic anions sometimes provide room-temperature molten salts (MS). These MS are quite stable against water and some kinds of these salts were even insoluble in water. Since MS was composed of only ions, this was expected to be highly ion conductive matrix. However certain MS were revealed to be excellent ion conductive matrices, their ionic conductivity was deeply affected by the structure of both cation and anion. Since there is no theoretical prediction on the structure of component ions for high ionic conductivity, tremendous efforts have been paid for the preparation and characterization of a series of salts. Polymerization of such MS is another interesting approach to obtain new types of polymer electrolytes[1-3]. Convenient preparation method of MS model compounds and their polymeric derivatives was also reported by us[4]. Polymerization of either cationic unit or anionic unit certainly reduced the ionic conductivity of the MS. The conductivity was considerably improved by the further addition of MS in spite of solid characteristics of the mixture. Their structure and conductivity will be reviewed.

[1] H. Ohno, Y. Nakai, and K. Ito, Chem. Lett., (1998) 15-16

[2] H. Ohno and K. Ito, Chem. Lett., (1998) 751-752

[3] Y. Nakai, K. Ito, and H. Ohno, Solid State Ionics, 113-115 (1998) 199-204

[4] M. Hirao, K. Ito, and H. Ohno, Electrochim. Acta, (2000) in press

PLENARY SESSION II

Chairpersons:

**Prof. Doug MacFarlane
Monash University, Australia
&
Prof. Steve Greenbaum
Hunter College of CUNY, USA**

ION TRANSPORT IN GLASSY POLYMER ELECTROLYTES

M.D. Ingram and C.T. Imrie

*Department of Chemistry, University of Aberdeen,
Aberdeen AB24 3UE, Scotland*

A recent advance in the field of polymer electrolytes is the discovery that ion transport occurs well *below* T_g in a variety of polymeric hosts [1,2]. This development indicates a radical departure from the conventional viewpoint that ionic motions are strongly coupled to segmental motions, and points the way forward: (i) to closing the conceptual gap between glassy and polymeric ionics; and (ii) to developing new strategies for optimising ionic conductivities in polymer electrolytes.

Instead of seeking ways to increase segmental mobility (and hence to lower T_g), it may be better to design new polymeric structures, which are stable in both the liquid and glassy states, and furthermore which resist the tendency to be reorganised on addition of salt. This alternative approach can be exemplified by reference to our own on-going investigations into the structure and properties of side-group liquid-crystal polymer electrolytes (SGLCPEs). Attention will be focused on our attempts at reaching optimum conductivities (conductivity increases progressively with increasing salt concentration), and at achieving a better understanding of how ion transport processes can become *decoupled* from structural relaxations of the host matrix.

- [1] H.A. Every, F. Zhou, M. Forsyth and D.R. MacFarlane, *Electrochim. Acta* **43** (1998) 1465.
- [2] C.T. Imrie, M.D. Ingram and G.S. McHattie, *J. Phys. Chem. B*, **103** (1999) 4132.

MECHANISMS OF TRANSPORT IN PROTON-CONDUCTING MEMBRANES FOR FUEL CELL APPLICATIONS

Thomas A. Zawodzinski Jr.¹, Stephen J. Paddison¹, Reginald Paul³, and Lawrence R. Pratt²

*Materials Science and Technology Division¹ and Theoretical Division²
Los Alamos National Laboratory, Los Alamos, NM 87545*

*³Dept. of Chemistry,
University of Calgary,
Calgary, Alberta, Canada*

We will present recent experimental and theoretical studies of proton and water transport and their coupling in proton conducting polymer electrolytes used in fuel cells. The starting point for this effort is a qualitative rationalization of observed transport data. The influence of various transport parameters on fuel cell operating characteristics will be described. We will compare and contrast mechanisms occurring in a series of polymers containing perfluorinated sulfonic acid and aromatic sulfonic acid moieties. We will describe computational studies that connect *ab initio* 'explicit water' calculations of sulfonic acid/water complexes to transport of protons along a pore or channel of ion-conducting polymeric materials. This model successfully calculates proton mobilities derived from conductivity experiments. We will discuss extensions of this work to obtain calculated values of solvation enthalpies for sulfonic acid sites and to show the influence of various structural and morphological features, such as pore diameter and sidechain length, on transport of protons through a pore. Finally, we will speculate on 'frontier' directions for preparation of new proton conducting membranes.

COMPUTER SIMULATION STUDIES OF STRUCTURE AND RELAXATION OF POLYMER ELECTROLYTES

Simon W. de Leeuw and Alex van Zon

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Faculty of Applied Sciences
Delft University of Technology
Lorentzweg 1
2628 CJ Delft*

Ionic conduction in polymer electrolytes is characterized by a strong coupling between the motion of ions and segmental relaxation of the polymer backbone. Using computer simulation techniques we investigate the structural behaviour of polymer electrolyte solutions and its relation to intermolecular interactions and the stiffness of the polymer backbone.

Structural relaxation is investigated through the coherent and incoherent intermediate scattering functions $F(k,t)$, which describe collective and diffusive motions of the polymer segments respectively. The coherent intermediate scattering function displays stretched exponential behaviour, which can be interpreted in terms of mode-coupling theory. The temperature dependence of the relaxation functions will be discussed. Addition of salt to the polymer strongly increases the relaxation time for structural relaxation of the segments with concomitant consequences for the ionic conductivity.

PLENARY SESSION III

Chairpersons:

**Prof. Simon de Leeuw
Delft University of Technology
The Netherlands**

&

**Prof. Michel Armand
Montreal University
Canada**

**NON-AQUEOUS PROTON CONDUCTING GEL ELECTROLYTES:
BASIC RESEARCH AND APPLICATIONS**

W. Wieczorek, G. Zukowska and R. Borkowska

*Faculty of Chemistry, Warsaw University of Technology, Noakowskiego str. 3, 00-664 Warszawa,
Poland*

The aim of this paper is to summarize recent trends in the studies on non-aqueous proton conducting gel electrolytes. The physical – chemical properties of these systems are described and their relation to the type and concentration of polymer matrix, proton donor as well as the solvent used is discussed. This analysis is performed on the basis of electrochemical (impedance spectroscopy, cyclic voltammetry), spectroscopic (NMR, PFG NMR, FT-IR), rheological and thermogravimetric (DSC) experiments. The proton conduction mechanism is postulated and its dependence on the sample composition is discussed. The possibility of application of proton conducting gels in electrochromic devices is presented.

Acknowledgments:

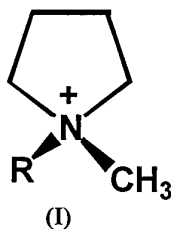
This work was financially supported by the State Committee for Research in the frame of the 3TO9B 087 13 and 134/E-365/SPUB-EUREKA/T-09/DZ024/ 98 and MEN/DOE-97-317 Research Grants.

POLYMER IN PLASTIC CRYSTAL ELECTROLYTES

Douglas R. MacFarlane* and Maria Forsyth[#]

*Departments of *Chemistry and [#]Materials Engineering
Monash University, Vic. 3800*

Recent work (1,2) has discovered that plastic crystal solid phases, such as the alkyl methyl pyrrolidinium (I) imide salts, can act as dopant hosts for small ions such as lithium. When doped with lithium ions such materials exhibit what we now believe to be fast-ion conduction of the lithium ion. These materials thus represent a new class of fast-ion conductor. The lithium ion conductivity observed ($>10^{-5}$ S/cm at room temperature) is sufficiently high that application in lithium batteries is a practical proposition. The mechanical properties of the doped plastic crystal are, as indicated by their nomenclature, plastic and, in order to provide some limitation to the extent of plastic flow under stress, we have begun investigating the binary mixtures of these salts with compatible polymers. These mixtures represent a sub-class of the much studied polymer-in-salt electrolytes, the polymer serving a similar but not identical role. This paper will describe the chemistry and properties of these new plastic crystal materials.



- (1) D.R. MacFarlane J. Huang and M. Forsyth, Fast Lithium Ion Conducting Doped Plastic Crystals; Solid State Electrolytes for Secondary Batteries., Nature 402 (1999) 792-794.
- (2) MacFarlane, D. R.; Sun, J.; Forsyth, M.; Meakin, P.; Amini, N. Pyrrolidinium imides: A New family of molten salts and conductive plastic crystal phases. J. Phys. Chem. 103, 4164-4170 (1999).

GEL ELECTROLYTES I

Chairpersons:

**Dr. Denis Fauteux
Pacific Lithium Ltd.
New Zealand**

&

**Prof. Bruno Scrosati
University of Rome, Italy**

GEL ELECTROLYTES – THE RELATIONSHIP BETWEEN CHARGE CARRIER MOBILITY AND STRUCTURE OF THE POLYMER

A. Reiche, A. Weinkauf, B. Sandner, G. Dlubek*,
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Lieskau, Germany*

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The dependence of electrochemical properties of gel electrolytes on the structure of the polymer is discussed for a number of gel electrolytes prepared by photopolymerization of appropriate monomers in the presence of various plasticizers, e. g. oligo(ethylene glycol)_n dimethylether ((EG)_nDME) and LiCF₃SO₃.

Heterogeneous gel electrolytes were formed by polymerization of e. g. oligo(ethylene glycol)_n dimethacrylate ((EG)_nDMA) with $n < 9$ or the alternating copolymerization of maleic anhydride with tetra (ethylene glycol) divinylether both in the presence of plasticizer and salt. Two glass transition temperatures were observed one of the plasticizer salt solution and one of the polymer, respectively, by dynamic mechanical analysis and differential scanning calorimetry. These gel electrolytes are characterized by high ionic conductivities presupposed that type and structure of the polymer provide the incorporation and optimal distribution of the liquid component. The cationic transference numbers are relatively high due to low interactions of the cations with the polymer [1].

Homogeneous gel electrolytes were obtained by polymerization of (EG)_nDMA with $n \geq 9$ as indicated by the observation of a single glass transition temperature. These electrolytes show usually lower conductivities than the gels above due to a lower realizable plasticizer content. The high ability of the polymer to interact with the Li⁺ ions results in a low contribution of cations to the charge carrier transport [1].

Despite the differences in the thermal and electrochemical properties of the various types of gel electrolytes studied low changes in the activation volume V^* estimated by pressure dependent conductivity measurements were found, $V^* \approx 20 \text{ cm}^3/\text{mol}$. These results were discussed in connection with the study of the free volume by positron annihilation lifetime spectroscopy and the morphology of the polymer by atomic force microscopy.

[1] A.Reiche, R.Sandner, A.Weinkauf, B.Sandner, G.Fleischer, F.Rittig, accepted for publication in POLYMER

**AMPHIPHILIC POLYMER GEL ELECTROLYTES.
INFLUENCE OF THE HYDROPHOBIC – HYDROPHILIC BALANCE
ON THE ION CONDUCTIVITY**

Ronnie Ljungbäck, Patrik Gavelin, Patric Jannasch and Bengt Wesslén

*Department of Polymer Science & Engineering, Lund University,
P.O. Box 124, SE-221 00 Lund, Sweden*

Gel electrolytes based on PMMA have shown high conductivity at ambient temperatures.¹ By introducing strongly hydrophobic groups in the polymethacrylate, and balancing the hydrophobicity by incorporation of hydrophilic segments, such as PEO, the ion conductivity of the gel electrolyte can be increased.² These amphiphilic graft copolymers may offer great flexibility in the design of polymer gel electrolytes for lithium polymer batteries.

In the present work, graft copolymers with different EO chain lengths and different EO contents were synthesized by radical copolymerisation of macromonomers. The hydrophobic content was varied by the inclusion of different amounts of fluoroalkyl methacrylates in the copolymer. Polymer gel electrolytes containing 30 wt % of the copolymers were prepared by using an electrolyte consisting of 1.0 M LiPF₆ dissolved in γ -butyrolactone.

The results, from several measurements, showed that introduction of short PEO grafts on a polymethacrylate backbone did not increase the ion conductivity significantly, as compared to PMMA. However, with the introduction of fluoroalkyl grafts in combination with PEO grafts, the ion conductivity increased substantially. The results also showed that the balance between the hydrophobic and hydrophilic parts of the copolymer strongly influenced the ion conductivity of the electrolyte. Furthermore, gel electrolytes based on amphiphilic copolymers containing PEO400 grafts had higher ion conductivity, as compared to copolymers containing diethylene oxide grafts, although the EO content was the same. The maximum ion conductivity measured at 20 °C were 2.4 and 4.0 mS/cm for amphiphilic copolymers containing di(ethylene oxide) and PEO400 grafts, respectively. Corresponding value for the unmodified polymethacrylate, that is PMMA, was 1.5 mS/cm.

References

1. G.B. Appetecchi, F. Croce, B. Scrosati, *Electrochimica Acta*, **40**, 1995 (8), 991.
2. P. Gavelin, P. Jannasch, B. Wesslén, *to be published*.

Acknowledgement

The financial support from the Swedish Foundation for Strategic Environmental Research, MISTRA, is gratefully acknowledged. The work was done within the framework of the Jungner Centre.

DIFFUSION OF SOLVENT/SALT AND SEGMENTAL RELAXATION IN POLYMER GEL ELECTROLYTES

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*Department of*Experimental and[#]Applied Physics,
Chalmers University of Technology, SE-412 96 Göteborg, Sweden*

Dynamic light scattering and broad band dielectric spectroscopy has been performed on polymer gel electrolytes consisting of a mixture of ethylene carbonate/propylene carbonate/lithium perchlorate (EC/PC/LiClO₄) and stabilised with a polymer matrix, poly(methyl methacrylate) (PMMA). The influence of the solvent and the salt concentration on the dynamical behaviour of the gel is presented. A complex relaxation behaviour is observed with multiple relaxation processes with different temperature and wave vector dependencies. The ionic conductivity mechanism is shown to be closely related to a fast diffusive process of low molecular weight compounds. A slower and very broad relaxation process is observed which has no wave vector dependence and is attributed to segmental motion of the polymer backbone. The temperature dependence of the relaxation processes is compared with the ionic conductivity with special emphasis on the relation between the fast diffusive process and the molar conductivity. It is found that the measured self-diffusion coefficient is in qualitative agreement with the diffusion of the ions as determined from the Stoke-Einstein relation. The physical picture that emerges from the results is that the conductivity mechanism is a diffusion of ions moving together with the solvent molecules and essentially decoupled from the segmental motion of the polymer backbone.

**STRUCTURAL PROPERTIES, THERMAL STABILITY AND ELECTROCHEMICAL
CHARACTERISTICS OF GEL POLYMERIC ELECTROLYTES BASED ON CHLORINATED
POLYVINYLCHLORIDE**

E. M. Shembel*, O. V. Chervakov*, A. G. Ribalka*, L. I. Neduzhko*,
D. Golodnitsky#, D.T.Meshri** and D. E. Reisner##

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School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel,
**Advance Research Chemicals, Inc., USA and ##US Nanocorp, CT, USA*

The properties of lithium-conducting gel polymeric electrolytes to a great extent determine a feasibility of secondary lithium batteries. The ionic conductivity in such electrolyte depends on its structural characteristics. Low-crystalline or amorphous polymers and their copolymers are used as the polymeric matrixes for the electrolytes in these batteries. In this work the results of the development and optimisation of the production technology of chlorinated polyvinylchloride (C-PVC) of increasing amorphous structure are presented.

The influence of the type of plasticizer, the lithium salt and the temperature on the conductivity of polymeric electrolytes has been investigated. Increasing the temperature causes instability in the polymeric matrix in the presence of lithium salts (especially reactive ones, such as LiPF_6 , LiBF_4 , LiSO_3CF_3 and others). Active cathode substances like MnO_2 , LiMn_2O_4 , FeS_2 and others behave in a similar manner. Their presence can result in side reactions of the polymeric material and hence adversely affect the operating characteristics of the developed electrochemical systems. With the use of X-ray diffraction and thermogravimetric analysis the influence of different lithium salts on the structural properties and thermal stability of polymeric electrolyte based on C-PVC has been estimated. The stability of this electrolytes decreases in the order of $\text{LiSO}_3\text{CF}_3 > \text{LiClO}_4 > \text{LiBF}_4 \sim \text{LiAsF}_6$.

The modification of the polymeric electrolyte in order to increase its thermal stability and ionic conductivity has been investigated. Tests of lithium accumulators containing polymeric electrolytes and the cathodes based on MnO_2 (3.0 V), LiMn_2O_4 , LiCoO_2 (4.0 V), FeS_2 (1.5 V) have been successfully carried out at ambient temperature.

Acknowledgements:

This work was carried out at financial support by STCU Grant #656 and CRDF Grant USB-384.

SOLVENT CONTAINING POLYACRYLIC NETWORK AS A SOLID ELECTROLYTE

T.I. Isaak and G. M. Morousov

*Department of Analytical Chemistry,
Tomsk State University, Tomsk, Lenina 36, Russia*

A new class of polymer networks for gel electrolytes crosslinked via hydrogen bond was specially designed and synthesized. The network was prepared by a radical copolymerisation methyl methacrylate with methacrylic acid (or its derivatives) in the presence of polyethylene glycol. This is a homogeneous transparent material.

By means of introduction of aprotic solvent (dimethyl sulfoxide, ethylene/propylene carbonate, dimethyl formamide) and electrolytic salt (LiCF_3CO_2 , LiCF_3SO_3) into a polymer precursor blend as a result of polymerisation a thermoreversible polymer gel electrolyte was obtained. It has bulk ionic conductivity higher than 10^{-4} S/cm at 293 K and 10 kHz. The melting temperature and the glass transition temperature are mostly defined by an amount of solvent and lies in the range of 325-340 K and 290-300 K accordingly. This gel has good optical properties too.

For the given network-solvent-salt system, the ionic contribution into the conductivity (99.9%) and transport numbers of ions was determined. The study of their range of electrochemical stability and the reduction potential of the lithium cation were carried out using the cyclic voltammetry techniques. These parameters are determined by a type of solvent and salt only. This fact proves that the polymer network is stable. A solid state lithium cell was prepared with this gel to prove its good performance.

GEL ELECTROLYTES II

Chairperson:

**Prof. Josh Thomas
Uppsala University, Sweden**

NEW POLYMER ELECTROLYTE FOR PLASTIC LITHIUM ION BATTERY

Jung-Ki Park and Nam-Soon Choi

*Department of Chemical Engineering,
Korea Advanced Institute of Science and Technology, 373-1, Kusung-dong,
Yusung-gu, Daejeon, 305-701, Korea*

The electrochemical properties of the polymer electrolytes based on poly(vinyl chloride)/poly(methyl methacrylate) blend with micropore structure have been investigated. The introduction of poly(methyl methacrylate)(PMMA) into poly(vinyl chloride)(PVC) matrix enhanced compatibility between the polymer matrix and the liquid electrolyte(EC/DMC/LiClO₄). The polymer matrix with micropore structure was obtained by extracting DBP from the polymer film containing silica and the polymer electrolytes were prepared by dipping the polymer matrix into the liquid electrolyte.[1] The addition of silica into the polymer blend generated micropore structure in the polymer matrix and increased the uptake amount of the liquid electrolyte. The ion conductivity of the polymer electrolyte was increased with the increase in the PMMA content in the blend and the room temperature ion conductivity of the polymer electrolyte based on PVC/PMMA(5/5, w/w) blend was 1.9×10^{-3} S/cm. The leakage of the liquid electrolyte from the polymer matrix was suppressed with the increase in the PMMA content in the polymer electrolyte due to the good compatibility of the polymer matrix with liquid electrolyte and the interfacial stability between the lithium electrode and the polymer electrolyte could be enhanced. The electrochemical stability window was also increased with the increase in the PMMA content and it was 5.1V for PVC/PMMA(5/5, w/w). The charge-discharge behavior of the unit cell was also investigated.

- [1] J.M.Tarascon, A.S.Gozdz, C.Schmutz, F.Shokoohi, and P.C.Warren, Solid State Ionics, Vol.86-88 (1996) 49-54

ION CONDUCTIVITY OF NOVEL POLYELECTROLYTE GELS FOR SECONDARY LITHIUM POLYMER BATTERIES

J. Travas-Sejdic, R. Steiner, J. Desilvestro and P. Pickering

Pacific Lithium Limited, Auckland, New Zealand

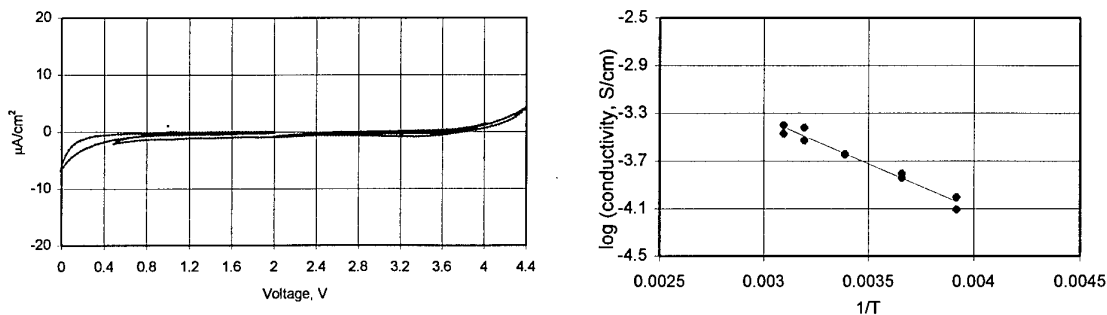
Polymer electrolytes that conduct lithium ion have attracted much interest due to their high potential for use in commercial rechargeable lithium polymer batteries. Lightness, design flexibility, ease of fabrication and safety are some of lithium polymer battery attributes. A number of thermoplastic polymers have been studied so far, such as PEO, PAN and PVdF copolymers, that act as hosts for plasticizer and Li-salt and form polymer gel electrolytes [1].

In comparison with above mentioned polymer gel electrolytes the polyelectrolyte gels offer the advantage of single ion conductivity due to the mobile cations and anions immobilized onto polymer network. That eliminates the need for additional salts and undesirable build-up of a resistive layer due to concentration polarization.

Here we report an ion conductivity study on a novel polyelectrolyte gel. The gel is Li-salt of cross-linked acrylamide-based copolymer. The monomers and solvent have similar chemical compositions that facilitate Li-ion dissociation and enhance ion conductivity. The copolymer gel is easily prepared by a simple free-radical copolymerization.

The ionic conductivity of the polyelectrolyte gel was studied by AC impedance spectroscopy using stainless-steel blocking electrodes in temperature range from approximately -20 to 50 °C. Obtained conductivity values lie in the range $1 \cdot 10^{-4}$ – $1 \cdot 10^{-3}$ S/cm. This will be compared with several 'conventional' gel systems containing dissolved LiCF_3SO_3 or LiPF_6 . Mechanistic aspects of Li-ion transport will be discussed in detail. Cyclic voltammetry was used to investigate the electrochemical stability window. Figure 1 shows that the gel is electrochemically stable in potential range from 0 to 4.4 V.

Figure 1. Cyclic voltammetry and Arrhenius plot of ionic conductivity of the polyelectrolyte gel.



[1] J.Y. Song, Y.Y. Wang, C.C. Wan, J. Power Sources 77 (1999) 183-197

THERMAL STABILITY INVESTIGATIONS ON PVDF- BASED NOVEL Li^+ CONDUCTING SOLID POLYMER ELECTROLYTE BLENDS FOR Li-ION BATTERIES

S.R.S. Prabakaran^{1*}, T.Y.Tou¹, Ramlee Adnan² and M.S. Michael³

¹*Center for Smart Systems and Innovations, Faculty of Engineering, Multimedia University, 63100 Cyber Jaya, Selangore, Malaysia.*

²*Foundation Studies and Extension Education, Multimedia University, 75450 Jalan Ayer Keroh Lama, Bukit Beruang, Melaka, Malaysia.*

³*Advanced Materials Research Center, SIRIM Bhd., Persiaran Dato' Menteri, Section 2, 40911 Shah Alam, Selangor, Malaysia*

A novel Li^+ conducting solid polymer electrolyte (SPE) was developed for lithium-ion batteries. PVdF was chosen to be the main polymer matrix together with PVK (polyvinyl carbazole) as a blending agent. The blend was prepared in a different weight ratio and optimized for a uniform blending without any phase secretion. The free-standing membranes were prepared using the casting procedure previously described by us [1]. The thermal effects were studied on the free standing membranes in the temperature range ambient up to 120°C by means of DSC/TG techniques. The optimized PVdF/PVK blend composition of 70:30 wt % was chosen to study the Li-salt/polymer composition in order to develop a highly conducting SPE. The impedance studies on the various salt/polymer blend composition (x) revealed an inverse parabolic trend with respect to σ_i . The maximum ionic conductivity of $\sim 10^{-4}$ S/cm at room temperature was achieved in (1M LiBF_4 + 2DMC/1EC) + PVdF/PVK blend. The details of the composition and conductivity behaviour will be presented.

[1] M.M.E. Jacob, S.R.S. Prabakaran and S. Radhakrishna, Solid State Ionics 104 (1997) 267-276.

ION DYNAMICS IN POLYETHER SOLID POLYMER ELECTROLYTES USING AC IMPEDANCE

P. Meakin¹, M. Forsyth² and D. R. MacFarlane¹

¹*Department of Chemistry, ²Department of Materials Engineering,
Monash University, Victoria, 3800 Australia*

The response of an electrolyte, as a function of frequency, f , to an applied small signal ac voltage is widely used in the conductive and dielectric characterization of electrolytes under development for innovative electrochemical devices. In order to gain an understanding and an insight of the microscopic processes occurring in the electrolyte the resultant macroscopic experimental data is analysed using one or a combination of the following related formalisms: complex conductivity, $\sigma(\omega)$ (where $\omega=2\pi f$), complex impedance, $Z(\omega)$, complex permittivity, $\epsilon(\omega)$ and complex electrical modulus, $M(\omega)$.

The choice of the formalism used to analyse the macroscopic data and its interpretation are the subject of a vigorous and as yet unresolved debate, particularly in the fast glassy ionic field. One of the contentious issues is the effect that the high frequency dielectric constant has on the resultant formalism analysis.

The aim of this study is to determine whether microscopic processes responsible for ion dynamics and structural relaxation can be determined from the macroscopic electrical measurement. The systems studied consist of a solid solvent polyether polymer lightly crosslinked with hexamethylene diisocyanate doped with a wide range of salt concentrations. Some of the SPE systems also contained plasticisers which decreased the microviscosity of the system and, with the appropriate choice of plasticiser, increase the permittivity of the system. The conductivity of SPEs (like all electrolytes) is determined by the mobility and number of ions which in turn is controlled by the concentration of the salt, the dielectric and structure of the polymer and plasticiser, if present. These factors determine the number dissociated ions, formation of ion pairs and ion clusters and mobility of the ions and structural relaxation. The motion of ions in SPEs, unlike that of the fast glassy ionics, is controlled by the segmental motion of the polymer backbone. The analysis of the isothermal electrical data was carried out using the different formalism levels and equivalent circuit methods. The systems were also studied at a set frequency to provide a landscape of the microprocesses occurring as a function of temperature. Thermal analysis was used to determine the onset of the alpha relaxation (segmental motion) of the SPEs and this was incorporated in the final analysis.

NEW SYSTEMS

Chairpersons:

**Dr. Anita Hill
CSIRO, Australia
&**

**Dr. Annette Reiche
Martin Luther University Halle Wittenberg
Germany**

ANION-TRAPPING POLYETHERS AND RELATED POLYMERS FOR S-IN-P, AND P-IN-S ELECTROLYTES

Xiaoguang Sun and C. Austen Angell

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We address the problem of low cation transport numbers in polyether polymers and polymers of other types, using a novel approach. The approach involves the incorporation of anion-attracting elements into the chain backbone. We have used the undercoordinated boron atom as the active element and, to date, have used weakly basic anions, SCN⁻, as the anions being trapped. Because normal polyether SPEs are principally anion conductors, this modification has the inevitable consequence of reducing the conductivity relative to those of simple polyether polymers with dissolved lithium salt. The lithium ion conductivity, however, is less affected. The effect of different boron atom concentrations in the polymer chain, and different salt concentrations in the polymer solution, will be reported.

Since the attraction of the boron for the anion provides a drive for dissolution of salt which is lacking in the normal polyethers, it should be possible to use polymers with less basic links than ether oxygens and still obtain adequate salt contents. In such polymers the cation mobility, as well as the cation transport numbers, should be more favorable. Thus there is some prospect of making salt-in-polymer electrolytes with higher conductivities than either the polyether-, or the boron doped polyether-, based systems. Such salt-in-polymer SPEs should have more favorable cation transport numbers than the usual cases. Our attempts to realize a class of salt-in-polymer electrolytes based on this principle will be described.

With a strongly basic anion incorporated, the polymer becomes an anionic polymer which should, in principle, be useful as the rubberizing ingredient in a polymer-in-salt electrolyte. Some tests of this conjecture will be reported.

NMR AND ION CONDUCTIVITY STUDIES OF A ETHYLENEOXIDE-PROPYLENEOXIDE
PRECURSER MONOMER DOPED BY $\text{LiN}(\text{SO}_2\text{CF}_3)_2$

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Since the diffusion phenomena of the ions in the cross-linked polymers were very complicated, the measurements of the T_1 , T_2 , and the self diffusion coefficients of the ^1H - ^{19}F - and ^7Li - NMR were made for the precursor monomer. The monomer structure is a glycerol derivative of ethylene oxide (EO) and propylene oxide (PO), the ratio being 8:2 and terminated by the methyl group. The molecular weight is about 8,000. The sample is liquid at the room temperature. We measured the NMR spectra for the pure solvent and the solution electrolyte doped by $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ with the mole ratio 20:1 by oxygen of the solvent and the Li.

The T_1 and T_2 (spin-echo) relaxation curves were all analysed by a single exponential for the lithium ion, anion, and solvent. The temperature dependent T_1 plots of the polymer and the lithium showed the minimum and the relaxation mechanism can be assumed by the dipole-dipole and the quadrupolar interactions for the ^1H and ^7Li NMR, respectively. The calculated correlation times indicate that the lithium motion is slower than the polymer motion. At the same temperature the correlation time of the pure solvent is faster than that of the electrolyte solvent.

The apparent self diffusion coefficients of the lithium, the anion and the solvent can be analysed as a freely diffusing particle but depend on the measuring parameter Δ . This trend becomes pronounced as the temperature decreases. Here we propose the model of the diffusion in the liquid system.

CONTROL OF LITHIUM TRANSFERENCE NUMBER BY USING LITHIUM SALT OF PERFLUORINATED POLYIMIDE COMPLEXED WITH POLYETHER

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A new methodology to obtain lithium-ion-conducting polymer electrolytes is proposed. Polymeric lithium salts, poly(2-oxo-1-difluoroethylene sulfonylimide lithium) (LiPEI) [1] and poly(5-oxo-3-oxy-4-trifluoromethyl-1,2,4-pentafluoropentylene sulfonylimide lithium) (LiPPI), have structures resembling recently developed highly dissociable imide salts, such as lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), and are considered as their polymer analogues. The polymeric salts were proved to dissociate in organic solvents by using complex impedance and pulse-field-gradient spin-echo (PFGSE) NMR spectroscopy. The electrochemical stability was similar to that of LiTFSI. Polymer electrolytes were prepared by dissolving LiPEI and LiPPI in polyether matrixes to afford compatible polymer alloys. Lithium transference number of the polymer electrolytes was found to be close to unity. The ionic conductivity was strongly dependent on the structure of the lithium salts and followed the order of LiTFSI > LiPPI > LiPEI, even at the same lithium concentration. The addition of a highly polar solvent, such as ethylene carbonate, to the polymer alloy electrolytes greatly enhanced the ionic conductivity.

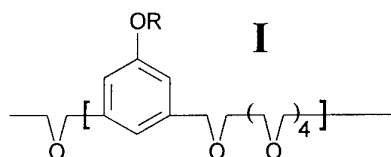
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HIGH AMBIENT DC AND AC CONDUCTIVITIES IN SOLVENT -FREE LOW-DIMENSIONAL POLYMER ELECTROLYTE BLENDS WITH LITHIUM SALTS

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Solvent-free polymer electrolytes have been prepared comprising LiClO_4 complexes with blends of poly[2,5,8,11,14-pentaoxapentadecamethylene(5-alkyloxy-1,3-phenylene)] (I) and random copolymers of poly(oxybutylene) coupled with various alkylene units



-(CH_2)₄ - O - A - (II)

The *n*-alkyl side chains R in I are either $-\text{C}_{16}\text{H}_{33}$ or a random equimolar copolymer mixture with $-\text{C}_{12}\text{H}_{25}$. The coupling units A in (II) are $-\text{CH}_2-$ or $-\text{CH}_2\text{C}(=\text{CH}_2)\text{CH}_2-$.

Conductivities over the range 1×10^{-4} to $6 \times 10^{-4} \text{ S cm}^{-1}$ at 20°C and $6 \times 10^{-5} \text{ S cm}^{-1}$ at -5°C have been observed in different systems of 50-100 μm films.

In I side groups R condense together in crystal or liquid crystal phases to create an ionophobic layer causing the polyether segments to generate a helical substructure [1]. Alkali metal cations occupy the helical tubes whilst the anions occupy spaces between the helices with lamellar long spacing 40 - 45 Å. X-ray crystallography, DSC, polarised light microscopy, molecular dynamics modelling and impedance spectroscopy indicate that strands of polymer II traverse the lamellae of I. When the films are sheared orientation of II promotes rotation and development of the conducting planes of I in the direction *normal* to the electrode substrate both in the bulk of the film and at the interface with the electrodes at a transformation temperature 80 - 110°C.

As in LB films of complexes of I [1], conductivities of the blends have low temperature dependence consistent with ions mobile through unimpeded channels in crystal and liquid-crystal phases with only weak coupling to the matrices.

1. P.V. Wright, Y. Zheng, D. Bhatt, T. Richardson and G. Ungar, *Polymer International*, 1998, **47**, 34.

ELECTROCHEMICAL AND PHYSICOCHEMICAL PROPERTIES OF POLYMER ELECTROLYTES CONTAINING ROOM TEMPERATURE MOLTEN SALTS

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Room temperature molten salts that have tetrafluoroborate anion [1] and bis(trifluoromethylsulfonyl)imide anion, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI), and 1-butylpyridinium tetrafluoroborate (BPF₄) and 1-butylpyridinium bis(trifluoromethylsulfonyl)imide (BPTFSI), were prepared, and characterization of these ionic liquids, such as thermal property, electrochemical stability, density, ionic conductivity, viscosity and diffusion coefficient, has been conducted. Pulse-gradient spin-echo NMR (PGSE-NMR) method was used to determine self-diffusion coefficient, and the results indicated that the cation and the anion in these ionic liquids diffuse almost equally. The relationship between the diffusion coefficient and viscosity is considered in terms of Stokes-Einstein equation, and the ionic conductivity and ionic mobility are discussed using Nernst-Einstein relation. Furthermore, in order to achieve highly conductive polymer electrolytes, *in situ* polymerization of vinyl monomers in the molten salts has been conducted. For example, 2-hydroxyethyl methacrylate network polymers in which BPF₄ is dissolved exhibit an ionic conductivity of 10^{-3} S cm⁻¹ at 30°C. In this system, although the glass transition temperature (T_g) is ca. 15 °C, the temperature dependence of ionic conductivity does not exhibit remarkable decrease below the T_g. These polymer electrolytes are assumed to be a decoupling system between structural relaxation and ion conduction. We will discuss about the ion transport mechanism of these polymer electrolytes by means of the PGSE-NMR and complex impedance methods.

[1] A. Noda and M. Watanabe, *Electrochim. Acta*, **45**, 1265-1270 (2000).

STRUCTURE AND CONDUCTIVITY IN POLYDIOXOLANE/LiCF₃SO₃ ELECTROLYTES

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Thermal transitions (T_g and T_m), ionic association and ionic conductivity have been measured as a function of LiCF₃SO₃ concentration of polydioxolane $(-\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-)_n$ based electrolytes. Thermogravimetric, DSC and X-ray diffraction measurements were performed on samples to which wt% lies between 0 and 58 wt%. The ionic association was investigated at room temperature for all compositions and the 30 wt% electrolyte was also studied between 23 and 70°C. The variation of conductivity with temperature has been fitted to the VTF equation $[\sigma = A \exp(-B/k(T-T_0))]$. It is found that (a) the T_g increases between -69°C and -44°C as a function of salt concentration up to 58 wt%; (b) the electrolyte is completely amorphous at 22 and 30 wt%; (c) the relative area of the Raman peaks associated with different ionic species indicates a pronounced increase of carrier numbers up to 30 wt% of salt, followed by a tendency to a "plateau"; and (d) the ionic conductivity at 300 K shows a large maximum value of $7 \times 10^{-5} \text{ S.cm}^{-1}$ between 12 and 48 wt%.

NOVEL POLYMER ELECTROLYTES WITH BORATE STRUCTURES AS ANION RECEPTORS FOR LITHIUM SECONDARY BATTERIES

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Polymer electrolytes are possible candidates for electrolytes of lithium secondary batteries, because the materials are expected to increase the safety, reliability, and energy density, and permit thin batteries with flexible geometry. However, the ionic conductivities at room temperature and the lithium ion transference numbers of polymer electrolytes are relatively low. Promoting the dissociation of lithium salts in polymer electrolytes by coordination of polymeric ligands with anions seems to be effective to increase the ionic conductivity and the lithium ion transference number. In order to reduce ion pairing in polymer electrolytes, we synthesized new types of monomers having tri-coordinate boron unit that functions as anion receptors. The polymer electrolytes having these anion receptors are expected to improve their characteristics because lithium cations are mobile whereas the anions are fixed on the polymer chain. When these monomers with borate structures were added in various organic liquid electrolytes containing lithium salts, ionic conductivities of the solutions were dramatically increased. In addition, we report the properties of polymer gel electrolytes prepared from the new monomers and a tri-functional macromonomer [1], incorporating different kinds of salts and solvents.

[1] M. Kono, E. Hayashi and M. Watanabe, *J. Electrochem. Soc.*, **146**, 1626-1632 (1999).

APPLICATIONS I

Chairpersons:

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&

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POLYMER ELECTROLYTE INTERFACES

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The use of polymer electrolytes in lithium rechargeable batteries was initially proposed in part because of their greater stability against lithium metal anode as compared to liquid electrolytes. It was originally expected that a polymer electrolyte could enable the efficient use of lithium metal anodes, preventing the formation of lithium dendrites during extensive cycling, and enabling the fabrication of very high energy density and safe rechargeable batteries.

Although the improved electrochemical stability provided by a polymer electrolyte is a real benefit inherent to the properties of polymer electrolytes, the emergence of a non-metallic anode enabling the lithium-ion system has provided a very efficient alternative to lithium anode based batteries. However, lithium anode systems are not absolutely stable against the electrolyte; "gazing" and "SEI" formation phenomenon are observed. It is understood that components of the liquid electrolyte are decomposed onto the surface of the carbon anode as the anode reaches a potential of approximately less than 1 Volt (against Li^+/Li^0) during the initial charge cycles. Parts of the decomposition products are gaseous species and parts are non-soluble oligomers that accumulate on the surface of the anode material thus forming the "SEI".

By analogy, one could argue that the "SEI" formed on carbon anodes in the lithium ion chemistry, are very efficient polymer electrolytes. One could also argue that such polymer electrolyte based "SEI" could be performed prior to the use of the anode material in the battery. In such case, the chemical composition, the thickness, and the ionic conductivity of the surface layer could be controlled. A direct consequence of this "control" will be to eliminate the gas producing reaction, consequently improving the reliability and safety of the lithium ion battery product. We will discuss the role of surface additives on the performance of carbon anodes in liquid and polymer electrolyte systems.

NEW POLYMER LITHIUM SECONDARY BATTERIES BASED ON ORMOCER® ELECTROLYTES (INORGANIC-ORGANIC POLYMERS)

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Based on new plasticized inorganic-organic polymer electrolytes [1] new flexible foil-batteries in "coffee bag arrangement" were assembled and tested. The electrolyte works as separator, and binder for the cathodes. Self-diffusion NMR studies on the system (EC/PC/Li⁺N(SO₂CF₃)₂/ORMOCER®) resulted in cationic transport numbers (t^+) of 0.42 for the EC/PC/salt system and 0.35 for the ternary electrolyte, typical for polymer electrolytes. Cycling tests (more than 900 cycles) proofed that the not plasticized electrolyte can act as binder electrolyte in composite cathodes of lithium secondary batteries [2]. Charge/discharge cycles of complete batteries like (Cu/active carbon/ORMOCER®/LiCoO₂/Al) with an ORMOCER® as separator electrolyte were measured. The voltage drop of these batteries is very similar to cells with standard liquid electrolytes and the efficiency is close to 100 %. Cycling the batteries with a current density of 0.25 mA/cm² between the voltage limits of 3.1 and 4.1 V results in a charge/discharge capacity (referring to the cathode mass) of 100 mAh/g at the beginning and after a slight decrease in a stabilised capacity of 75 mAh/g after 15 cycles. These promising results could be optimised by using highly purified components.

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- [2] S. Skaarup, K. West, B. Zachau-Christiansen, M. Popall, J. Kappel, J. Kron, G. Eichinger and G. Semrau, "Towards Solid State Lithium Batteries Based on ORMOCER® Electrolytes, *Electrochimica Acta*, 43, (1998), 1589.

HUMIDITY SENSOR BASED ON ALKALI SALTS OF POLY(2-ACRYLAMIDO-2-METHYLPROPANE SULFONIC ACID)

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Various types of polymer electrolytes have been used to develop resistivity-type humidity sensors. Most of the commercialized humidity sensors of this type are based on the polymer electrolytes having quaternary ammonium group as a hydrophilic site. In the present study, poly(2-acrylamido-2-methylpropane sulfonic acid) and its alkali salts were used to fabricate the sensor devices. Uniform polymer films (3 mm) were prepared by spin coating aqueous solution of the polymer on the surface of an alumina substrate having a pair of interdigitated gold electrodes. Humidity dependence of the impedance was measured in the range of 100~1MHz at 25°~50°C and the complex impedance analysis was carried out on the basis of the assumption of an equivalent circuit of a parallel combination of the resistance and the capacitance. The value of the activation energy for the resistance is in the order of $H < Cs < Rb < Na$ salt. The activation energy also depends on the amount of sorbed water. The value of impedance of these devices is in the order of $H < Cs < Rb < K < Na < Li$ salt, while the number of sorbed water molecule per monomer unit is in the order of $H > Li > Na > K > Rb > Cs$ salt. When the sensors are kept at 98%RH at 25°C for 500 hrs, the acid form deteriorated to some extent while Cs form is quite stable. A modified polymer film using IPN formation method is proposed to fabricate a sensor which can be operated at high humidity where dew drops may appear on the surface of the sensor.

SOLID POLYMER ELECTROLYTES: THE LIMITING FACTOR IN POLYMER ACTUATOR PERFORMANCE

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The development of highly efficient electromechanical devices based on functional polymers requires the design and construction of efficient solid state electrochemical cells.

In our laboratories the use of two types of actuating electrodes is under investigation. The first involves inherently conducting polymers such as polypyrroles, whilst the second involves the use of carbon nanotubes. With the former system actuation is achieved via dimensional changes in the polymer induced by ion incorporation / exclusion as the polymer is reduced or oxidised. In the nanotube system these dimensional changes are induced by a quantum chemical effect as the nanotubes are charged and discharged to form / remove an electric double layer. With both systems the nature and mobility of the ions employed plays a critical role in determining the overall performance of the polymer actuator.

The development of all solid state devices therefore requires the identification and / or development of solid polymer electrolytes that can accommodate ions that maximize the actuation effect. In the course of our work a number of solid polymer electrolytes based on polyacrylonitrile, Kynar or polyethylene oxide as well as polyacrylamide gels have been investigated and compared.

Using these results the properties required of the ideal solid polymer electrolyte for use in artificial muscles have been elucidated.

APPLICATIONS II

Chairpersons:

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&
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Monash University, Australia**

POLYETHER ELECTROLYTES FOR LITHIUM BATTERY APPLICATIONS

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Amorphous polyether–lithium salt complexes have been studied as potential electrolytes in lithium batteries. These systems undergo no thermal transitions between *ca.* -50°C and 100°C and exhibit conductivities in the range of 10^{-5} Scm^{-1} at 20°C to 10^{-4} Scm^{-1} at 60°C ; properties highly desirable for polymer battery applications. The polymer electrolytes have been studied in two types of half cell comprising lithium-intercalating graphite anode *vs* Li/Li^{+} ("anodic" half cell) and spinel lithium manganese oxide cathode *vs* Li/Li^{+} ("cathodic" half cell). Galvanostatic charging and discharging of the half cells was used to investigate cycling stability and capacity loss. Cathodic half cells were cycled between 3.5 V and 4.5 V *vs* Li/Li^{+} , and the anodic half cells between 1.5 V and 10 mV *vs* Li/Li^{+} . The electrochemical stability of the polymer electrolytes was determined using three-electrode cyclic voltammetry. Raman spectroscopy and DSC measurements were used to study changes in the electrodes and electrolytes during cycling. The effects of cell cycling at elevated temperature and of plasticising the polymer electrolyte systems were also investigated.

**STRUCTURAL EVOLUTION AND CONDUCTIVITY
OF PEO:LiBF₄-MgO COMPOSITEE ELECTROLYTES**

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This paper explores and proposes a structure-conductivity correlation in the PEO:LiBF₄-MgO composite electrolyte system. The proposed correlation is derived from interpretations of DSC and conductivity measurements. Thermal cycling in the 0 to 100°C range yields an amorphous polymer structure believed to be beneficial for enhanced conductivity. The proposed roles of MgO are to depress the PEO melting temperature and retard the kinetics of its crystallization. A resistivity relaxation or conductivity enhancement below the melting temperature of PEO (68°C) occurs, which appears to be a characteristic of these electrolytes and related to an interaction of dipoles associated with polymer chains and MgO. A higher concentration (~30%) of MgO leads to its segregation and reduction in conductivity resulting from crystallization of PEO.

ELECTROCHEMISTRY OF PLANAR SOLID-STATE AMPEROMETRIC DEVICES BASED ON NAFION AND POLYBENZIMIDAZOLE (PBI) SOLID POLYMER ELECTROLYTE

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Electrochemical gas sensors offer a cheap, easy to use and portable means of gas monitoring. In recent publications we have demonstrated the feasibility of using an alternative type of electrode arrangement in all-solid amperometric gas sensors based on a solid polymer electrolyte [1,2]: both the working and counter (and reference) electrodes are deposited on the same face of the electrolyte substrate and are in direct contact with the gas sample. Current distribution considerations due to electrode arrangement and electrolyte conductivity (as well as consideration of the electrode layer thickness for non-porous electrodes) dictate that the gaseous analyte reacts at or close the metal layer edge, at the metal/gas/solid polymer electrolyte interface. The main advantages of this planar sensor design would be its non-labour-intensive fabrication and the high mass transport rates of the analyte to the sensing electrode/electrolyte interface.

The principle of using such a device for amperometric gas detection was tested using vacuum-deposited non-porous Au/Nafion®/Au devices for oxygen determination. In this communication, the design is extended to a polybenzimidazole (PBI) based sensor and other types of electrode deposits, such as lines of porous Pt/C catalysts. Furthermore, practical issues of these sensors including maintaining the polymers' water content, long-term signal stability and the possibility of using them as two-electrode devices are also addressed.

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[2] K.Wallgren and S. Sotiropoulos, *Sensors and Actuators B: Chemical* 60, 2-3 (1999) 174-183

DISCHARGE STUDIES OF POLYMER ELECTROLYTE BASED ELECTROCHEMICAL CELLS

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Polymer electrolytes are widely used due to their Physical and chemical nature [1]. Initially the metal electrodes were used, later intercalation electrodes are used in order to obtain high energy density batteries [2]. Based on these reports, different working conditions of a new polymer electrolyte (PEO:NaClO₃) electrochemical cells are fabricated with different electrodes (Sodium iodide salt, Iodine, MnO₂ and Na_xMn₂O₄). This polymer electrolyte has an ionic conductivity of 2.38×10^{-5} S/cm at 30°C. The cells were fabricated with the configuration of NaI, Na_xMn₂O₄ | Electrolyte | I₂, MnO₂. Their discharge characteristics were studied at room temperature (30°C). From the cell parameters, the open circuit voltage (OCV) ranges from 680 mV to 1300 mV and short circuit current (SCC) ranges from 45 µA to 535 µA. We have also studied the plasticizing effects on the electrodes.

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[2]. J.R. Owen, A.L. Iasker and S.Chandra, *Superionic Solids and Solid electrolytes- Recent Trends*, Academic Press, New York (1989) 111.

**AN ALL SOLID-STATE PHOTOELECTROCHROMIC WINDOW
WITH POLY(ETHYLENE OXIDE) (PEO) GEL ELECTROLYTE**

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Intensified research efforts to develop electrochromic devices have spread worldwide in recent years. The focus of these research programs is on large area window applications. For such applications, all solid state electrochromic devices have unique advantages (such as reliability and safety) when compared to conventional liquid-based devices. Although electrochromic windows can be employed to provide user control of light transmission, such devices require an externally applied voltage to control the electrochromic behaviour of the device. The requirement for wiring every window into the building's electrical mains adds significantly to the production cost, particularly if the electrochromic window is being retrofit into an existing building. By incorporating a photovoltaic power source into the electrochromic window, however, this wiring cost could be reduced or eliminated, and the installation of the electrochromic window could be greatly simplified. In previous papers, we described the photovoltaic behaviours of dye sensitized TiO_2 microporous electrodes and fabrication of an all solid-state electrochromic smart window with polymer gel electrolyte with high conductivity (1mS/cm) at room temperature. A combination of a dye-sensitized TiO_2 solar cell, a PEO gel electrolyte and an electrodeposited WO_3 thin film to produce a novel all solid-state photoelectrochromic window will be demonstrated here. The photoelectrochromic window has been excellent for chromism and memory characteristics. Even in the presence of radiation, the photoelectrochromic window can be bleached by application of an external voltage after the device has been darkened.

THEORY/SPECTROSCOPY I

Chairperson:

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Arizona State University, USA**

APPLICABILITY OF FREE VOLUME THEORIES TO MECHANISMS OF CONDUCTION IN POLYMER ELECTROLYTES

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Free volume theories have been used to model or discuss ion mobility in polymer electrolytes, polymer-in-salt-electrolytes, and plastic crystals. Investigation of free volume by positron annihilation lifetime spectroscopy of several polymer/salt binary systems allows a critical review of the applicability of free volume theories to mechanisms of conduction. Positron annihilation lifetime spectroscopy provides a measure of nano-void size and concentration. Comparison of the free volume-conductivity relationships in rubbery and glassy polymer electrolytes, polymer-in-salt-electrolytes, and plastic crystals is made. The data support a contribution from free volume in charge carrier mobility for rubbery electrolytes where ion-polymer interactions are important to conductivity; however, a decoupling of the ion-polymer dynamics in glassy electrolytes and PISE leads to a diminished role of free volume in ion transport. The concentration of lattice vacancies resulting from rotational disorder in plastic crystals is held responsible for the conductivity via ion hopping between vacancies.

**A COMPARATIVE VIBRATIONAL SPECTROSCOPIC STUDY OF LITHIUM TRIFLATE
AND SODIUM TRIFLATE IN LINEAR POLY(ETHYLENEIMINE)**

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Systems of linear poly(ethyleneimine), LPEI, with dissolved sodium triflate (NaTf) and lithium triflate (LiTf) have been studied via Raman and infrared spectroscopy. The host LPEI polymer was synthesized via acid hydrolysis of 200,000 MW poly(2-ethyl-2-oxazoline), producing high molecular weight LPEI in good yield. Samples of LPEI/lithium triflate were prepared in a concentration range of 4:1 to 40:1 (nitrogen:sodium). Both LiTf and NaTf exist as ion pairs and more highly associated species in the LPEI system, with the degree of ionic association increasing with increasing salt concentration. It is also observed that addition of lithium triflate or sodium triflate breaks hydrogen bonds in LPEI and results in local conformational changes in the polymer.

OPTICAL ABSORPTION SPECTRA AS A LOCAL STRUCTURAL PROBE OF PEO

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POLYMER materials are widely expected to underlie many of the innovational technologies of the 21st Century. Equally, OPTICAL materials are due for a dramatic development within their many ranges of application over the coming decades. These two trends merge in the area of LUMINESCENT POLYMERS, typically for novel optical displays, detectors, fluorescent lighting and for a diversity of opto-electronic applications. It is relevant, therefore, to acquire a deeper understanding of the intuitively apparent structure-property relationship in these types of material. To this end, Molecular Dynamics (MD) simulation of a physically realistic sequence of rare-earth (RE) ion environments in these luminescent polymers provides the essential structural basis for the calculation of their optical properties, especially of their UV-VIS absorption and emission spectra.

In the work reported here, state-of-the-art MD simulations are made for Er(III) ions dissolved in an amorphous PEO host; the salts used in the spectral calculations are Er(III)Cl₃ and Er(III)(CF₃SO₃)₃, for Er:EO ratios 1:4, 1:7 and 1:10. Particularly in the triflate case, considerable effort must be made to prepare appropriate potentials for the simulation. The spectra are evaluated by calculating the field experienced by each RE ion in the chosen simulation box and, from this, extracting the effective oscillator strengths for the electric-dipole transitions within the 4f¹¹ configuration for each individual ion [1]. The entire spectrum is derived by accumulating the contributions (in sums made over space and time) from all Er(III) ions in the box. The results obtained from applying the method will be demonstrated and, if possible, compared with experiment.

[1] M. Klintenberg, S. Edvardsson & J.O. Thomas. *J. Alloys and Compounds*, 275-277 (1998) 174.

A ROUSE MODEL FOR POLYMER ELECTROLYTES

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A generalization of the Rouse-model, able to describe randomly cross-linked polymers, is used to model polymer backbone dynamics and ionic conductivity in poly(ethylene-oxide) (PEO) NaI polymer electrolytes above the glass transition temperature. In these calculations it is assumed that each Na ion forms a permanent cross-link between two oxygen atoms of the PEO backbone. In this way a coupled set of Langevin equations is constructed similar to the Rouse model for linear polymer chains. By calculating the eigenvectors and eigenvalues of the Rouse matrix, the self part of the intermediate scattering function $F(k,t)$ and the frequency dependent ionic conductivity are obtained.

We find that under the influence of cross-links, the relaxation times of $F(k,t)$ increase, indicating a slowing down of structural relaxations. Also, when fitted with a stretched exponent, we observe a decrease of the stretching parameter β . Both observations are in qualitative agreements with the results of neutron spin-echo experiments and molecular dynamics simulations on the ps/ns timescale. The frequency dependent conductivity is also in agreement with experimental results. These observations suggest that on this timescale, the conductivity is mainly determined by the cooperative motion of the polymer-ion complex.

THEORY/SPECTROSCOPY II

Chairpersons:

Prof. Jung-ki Park
Korea Advanced Institute of Science &
Technology, Korea
&
Prof. Malcolm Ingram
University of Aberdeen, United Kingdom

NEW LITHIUM SALTS ON THE COMPUTER: FICTION OR FACT?

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The need for new lithium salts for usage in the traditional salt/polymer polymer electrolytes is still urgent. The presently used lithium salts all have some limitations. How can we find the most suitable new salts? We here use *ab initio* quantum mechanical calculations as a primary selection tool. Calculations have been made on isolated anions, 1:1 ion-pairs with lithium as the cation, and 1:1:1 oligomer-cation-anion complexes. Properties calculated include binding strengths, charge distributions, thermodynamic stabilities, vibrational spectra... The combined picture from the calculations gives valuable information, which can (and should!) be compared to existing experimental data.

Calculation results for "traditional" polymer electrolyte salts like LiBF_4 , LiClO_4 , LiPF_6 , LiTFSI , and their usage in poly (ethylene oxide) (PEO) based systems, are presented. The results are compared to experimental studies with focus on vibrational spectroscopy to elucidate the local coordination environment.

The experience gained is then applied to new lithium salts, some of which only "exists" on the computer desktop. The salts of our current most interest are presented and discussed. Of course, the ultimate goal is to be able to predict which anions, out of these "imaginary" salts, will provide the lowest total lithium ion coordination strengths and thereby the highest ion conductivities in real polymer electrolyte systems.

**A VIBRATIONAL SPECTROSCOPIC STUDY OF LITHIUM TRIFLATE IN
POLYPHOSPHAZENES WITH LINEAR OLIGOETHYLENEOXY SIDE CHAINS OF
DIFFERENT LENGTHS**

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*[#]Department of Chemistry
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A comparative spectroscopy study has been undertaken on a series of polymer electrolytes composed of poly(oligoethyleneoxy phosphazenes) containing dissolved lithium triflate. These polymers, of the form $[NP((OCH_2)_xOCH_3)_2]_n$, where $x = 0, 1, 2$ or 5 , have been mixed with lithium triflate in concentration ratios ranging from 2:1 to 40:1 monomer unit:lithium triflate. Infrared and Raman vibrational spectroscopy have been used to examine ionic association and local conformational changes of the ethoxy side chains as the salt concentration and side chain length vary. The degree of ionic association of the triflate ion increases with increasing salt concentration. Local conformational changes of the oligoethyleneoxy side chains upon the addition of lithium triflate are dependent on the length of the side chains.

MOLECULAR DYNAMICS SIMULATION OF THE "PLASTICIZING" EFFECT OF Al_2O_3 NANO-PARTICLES ON ION TRANSPORT IN THE PEO-LiCl SYSTEM

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It has been established, *cf.* [1], that the addition of "solid plasticizers" in the form of nano-size inorganic particles of TiO_2 , SiO_2 , Al_2O_3 , *etc.* to a PEO-LiX polymer electrolyte has an enhancing effect on ion transport. What is not so clear, however, is the underlying origin of the effect. Logically, we can suspect that it is simply a "particle-size" effect which, more or less efficiently, suppresses tendencies towards local order ("crystallinity") in the PEO-LiX system. The fact that little direct evidence yet exists on this point constitutes an ideal motivation for attempting to perform a Molecular Dynamics (MD) simulation of the situation for different size particles, salt concentrations, *etc.*, and thereby establishing some idea of the relevant parameters which control the enhancement mechanism.

To this end, we have embarked upon the simulation of the system PEO-LiX- Al_2O_3 : particle diameters are 13, 17 and 22 Å (larger particles incur mitigatingly high computation times, while such small particles provide the possibility of magnifying the enhancement effect). One such particle is placed in an MD box of amorphous PEO, to which LiX is then added. Box sizes range from 30x30x30 to 60x60x60 Å. Conventional MD simulation is performed involving the usual features: initial thermal equilibration, periodic boundary conditions, Ewald summation, *ca.* 1ns sampling times, *etc.* Potentials are taken to a large extent from our earlier work [2]. The Al_2O_3 particles were created by "cutting" appropriate pieces from an α - Al_2O_3 (corundum) crystal, and then computer-annealing them at 2000K to achieve a more rounded shape and O-atoms situated on the outer surface. It is expected that at least preliminary results from these simulations can be presented.

[1] F. Croce *et al.* *Nature*, 394 (1998) 456.

[2] S. Neyertz, D. Brown & J.O. Thomas. *Comp. Polymer Science*, 5 (1995) 107.

DIFFUSION IN NOVEL SALTS

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The conductivity limitations in polymer electrolytes have resulted in a shift towards developing highly concentrated electrolytes based on novel salts. Salts with an imidazolium or pyrrolidinium ring are just two of the families that have been the focus of current research. The 1,3-methylalkylimidazolium iodide or bromide with methyl and ethyl substituents exhibit melting points above 350K. Conductivities in these materials were found to be of the order of 10^{-3}Scm^{-1} at 303K and 10^{-2}Scm^{-1} above the melting points. Analysis of the cation diffusion behaviour also showed uncharacteristically high coefficients of the order of $10^{-11}\text{m}^2\text{s}^{-1}$ at 303K. Such diffusion coefficients are comparable to similar salts in the liquid state. A change in activation energy for the cation diffusion occurred near the melting point which suggests a change in the transport mechanism.

The 1-ethyl-1-methylpyrrolidinium imide salt melts at 360K and has a reasonably low ionic conductivity of 10^{-8}Scm^{-1} at 303K. However, the addition of small amounts of lithium imide (0.9mol%) to the pure salt results in an increase in conductivity of well over an order of magnitude. Adding almost 5mol% lithium imide results in a conductivity of 10^{-5}Scm^{-1} at 298K. The mobility of this salt has been characterised as a function of temperature using NMR diffusion techniques. The results of these experiments and the measurements on the imidazolium salts will be discussed further in this presentation.

COMPOSITES AND PROTON CONDUCTORS

Chairpersons:

**Prof. Masayoshi Watanabe
Yokohama National University, Japan**

&

**Dr. Patrik Johansson
Chalmers University, Sweden**

LITHIUM AND PROTON CONDUCTING GEL-TYPE ELECTROLYTE MEMBRANES

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Large interest in is presently devoted to the development of gel membranes and to their use in advanced-design, plastic-like electrochemical devices. In our laboratory we have demonstrated the validity of this approach for the case of lithium ion conducting membranes, e.g., membranes formed by the immobilization of mixed organic solutions of lithium salts in a polymer matrix. Relevant examples are membranes formed by the gelification of a LiPF_6 ethylene carbonate-dimethyl carbonate, EC-DMC, solution into a poly(acrylonitrile), PAN matrix. In this paper, in addition of reporting the characteristics of some selected examples of lithium membranes, we demonstrate that the gel approach can be extended to other ion conducting membranes. In particular, we report the properties of new types of protonic membranes formed by the inclusion of mixed solvent solution of an organic acid in a poly(methylmetacrylate), PMMA matrix. The results confirm that the gel forming procedure, so far mainly addressed to the fabrication of lithium conducting membranes, may indeed be extended to other ionic polymer systems.

A HETEROPOLYACID-POLYMER PROTON CONDUCTOR FOR APPLICATION IN POLYMER ELECTROLYTE FUEL CELLS

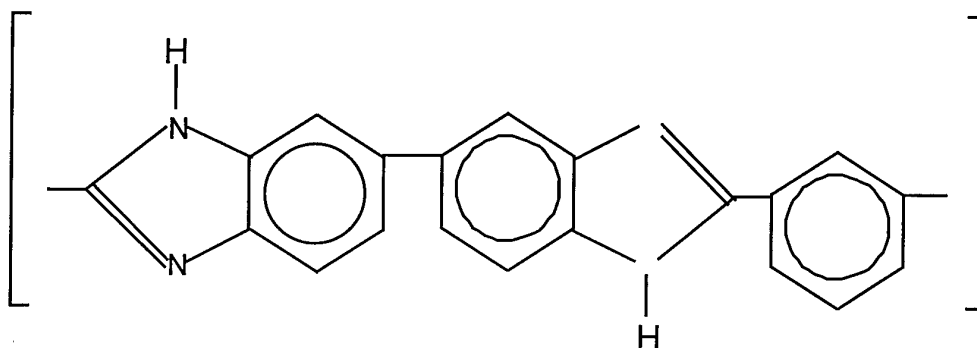
L. Jordan¹, D.R. MacFarlane², I. Bugar³ and M. Forsyth¹

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The very high proton conductivity, in solid heteropolyacids (HPAs) such as phosphotungstic acid ($\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3 \cdot x\text{H}_2\text{O}$) and silicotungstic acid ($\text{H}_4\text{SiO}_4 \cdot 12\text{WO}_3 \cdot x\text{H}_2\text{O}$) (STA) has resulted in their investigation for use as electrolytes in polymer electrolyte fuel cells. The high solubility of HPAs in water, however, limits their use as solid electrolytes in low temperature fuel cells since water is produced during fuel cell operation.



PBI

In this work polybenzimidazole (PBI) - silicotungstic acid (STA) was investigated as a proton conducting polymer electrolyte. The solvent based reaction of silicotungstic acid and polybenzimidazole produced a precipitate that was found to be insoluble in water and dimethylacetamide. FTIR and NMR spectra indicate that the interaction of STA with the polymer results in strong ionic bonds via protonated N groups on the polymer and the STA anion.

The insolubility of the material is a very important result for use in polymer electrolyte fuel cells however the specific conductivity is several orders of magnitude lower than that of fully hydrated STA ($29\text{H}_2\text{O}$) suggesting some inhibition of proton diffusion in STA. This loss of conductivity is discussed in terms of STA anion valency as well as percolation limitations and suggestions for enhancement of the conductivity will be presented.

NANO-STRUCTURE OF NAFION: A SAXS STUDY

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We performed small angle scattering experiments with synchrotron radiation [1] to study the nano structure and the swelling behaviour of NAFION polymer membranes under in situ measurement conditions, which are relevant for their use in direct methanol fuel cells. In pure water, a water-methanol mixture and in pure methanol.

To retrieve structural information from the scattering data, we apply a structure model with hydrophobic backbone material inside of platelet like, about 0.8 nm thick regions, which are surrounded by a hydrophilic ion and water group rich layer with a shell thickness of about 1.7 nm and a slight trend of shrinking for the methanol flooded sample. In summary, the scattering data indicate, that simple structure models with anisotropic basic structure units can be applied to describe the nanostructure of ionomers like nafion.

[1] H.-G. Haubold et al., Sci. Instr. **60**, 1943-1946 (1989)

THE ROLE OF THE INORGANIC OXIDE IN NANOCOMPOSITE
POLYMER AND GEL ELECTROLYTE STRUCTURE AND ION
TRANSPORT MECHANISM: AN NMR STUDY

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The addition of nanoscale inorganic powders (e.g. Al_2O_3 , SiO_2) to polymer and gel electrolytes has been shown to improve mechanical and electrochemical properties. In the case of solvent-free, PEO-based polymer electrolytes for Li battery development, the finely divided inorganic component tends to inhibit the formation of crystalline phases, thus leading to a more highly conductive material. There is also recent evidence that interactions between the metal oxide surface and the polymer and/or salt may affect the ion transport mechanism. In the case of gel electrolytes, the inorganic oxide component plays a vital role in providing a mechanical framework that allows maximum uptake and stabilization of the liquid electrolyte component. This presentation summarizes recent activity on two classes of materials: (i) PEO: LiClO_4 composites containing nanoscale Al_2O_3 or TiO_2 ; (ii) highly proton conducting gels consisting of poly(vinylidene fluoride), propylene carbonate, KOH, and nanoscale Al_2O_3 . Both ^7Li and ^1H NMR were utilized to investigate the local environment about the mobile ions with particular emphasis on the effect of the added metal oxide component. The extent of surface interactions between metal oxide and polymer was studied by ^{27}Al NMR. Finally lithium and proton self diffusion coefficients in the nanocomposite materials were determined by pulsed field gradient NMR and correlated with electrical conductivity data.

IONIC CONDUCTANCE BEHAVIOR OF POLYMERIC COMPOSITE SOLID ELECTROLYTES CONTAINING LITHIUM ALUMINATE

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In order to obtain high ionic conductivity without any low molecular-weight component, we have adopted a solid composite that contains a cross-linked polymer network, high concentration of lithium salt and an inorganic filler. The polymeric composites consisting of poly(ethylene oxide)-grafted poly(methylmethacrylate) (PEO-PMMA) with ceramics filler have been prepared by photo-induced radical polymerization of methacrylate monomers which dissolve lithium salts and disperse lithium aluminate (LiAlO_2) fine particles. The ionic conductivity was enhanced by dispersing the ceramics particles over a wide temperature range. As high conductivity as $10^{-5} \text{ S cm}^{-1}$ was obtained for the composite of (PEO-PMMA)/ LiClO_4 / LiAlO_2 without any plasticizing component. The optimum amount of the ceramics was around 3 wt% for the system. The addition of the ceramics to the (PEO-PMMA)/ LiCF_3SO_3 system gave a smaller effect than in the LiClO_4 system. XRD measurements of the polymeric solid electrolytes showed that the dispersion of LiAlO_2 increases the fraction of an amorphous phase in the composites. However, DSC and Raman spectra experiments did not reveal any significant structural changes when the ceramics filler was added in the polymeric electrolyte system. The Li^+ transport characteristics in the solid, which was examined by ^7Li NMR, were slightly affected by the addition of the LiAlO_2 particles in the (PEO-PMMA)/ LiClO_4 system.

NMR AND DSC STUDY OF PEO-BASED COMPOSITE POLYMER ELECTROLYTES

A.C. Bloise¹, C.C. Tambelli¹, R.W.A. Franco¹, C.J. Magon¹,
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Composites polymer electrolytes of poly(ethylene oxide) (PEO), LiClO₄ ([O/Li] = 8) and particle fillers were investigated by differential scanning calorimetry (DSC), conductivity and nuclear magnetic resonance (NMR). Composites were prepared by the solvent casting technique using α -Al₂O₃ (surface area 10 m²/g; average particle size 300 nm), γ -Al₂O₃ (200 m²/g; 4 μ m) and *Carbon Black (CB)* (Black Pearls, 1475 m²/g; 12 nm). All composites were prepared with 20 wt. % of filler concentration using an ultrasonic finger to ensure particle dispersion. NMR line shapes and spin-lattice relaxation times (T_1) of ¹H and ⁷Li were measured at the Larmor frequency of 36 MHz (¹H) and 155.4 MHz (⁷Li), in the temperature range 180 - 380 K. Single ¹H and ⁷Li T_1^{-1} maxima were observed for all samples. Activation energies obtained from the ⁷Li relaxation data are in the range 0.20 - 0.26 eV. Exponential ⁷Li relaxation was observed for the composite prepared with CB throughout the investigated temperature range. For the composites prepared with α - and γ -Al₂O₃, ⁷Li relaxation is non-exponential only below 270 K. The onset of the ⁷Li line-narrowing and the relaxation rate maxima (T_1^{-1})_{max} was observed to occur at lower temperatures for the composite prepared with α -Al₂O₃. These results suggest that the lithium mobility is higher in the composite prepared with α -Al₂O₃ particles than in the unfilled PEO₈LiClO₄ and composites prepared with CB and γ -Al₂O₃.



POSTER SESSION I

Monday 7th August
5.20pm – 6.45pm

NANO-COMPOSITE ELECTROLYTES FOR USE IN NOVEL LITHIUM BATTERY APPLICATIONS

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Currently, electrolytes for use in Magnetic Pulse Compacted (MPC) all-solid state lithium batteries have an optimal operation at temperatures near 180°C. [1] The electrolytes consist of a Li doped BPO₄ ceramic within an inactive binder of PVDF. [2] In order to decrease the operating temperature of the battery, without affecting the conductivity of the electrolyte, the use of a suitable lithium ion conducting polymer is proposed instead of the PVDF.

We will present results of polymer electrolyte composites of PEO ($M_w = 600,000$ g/mol) 2.8 mol/kg LiClO₄, aPEO ($M_w = 27,000$ g/mol) 2 mol/kg LiClO₄ and 3PEG (a polyether triol with a molecular weight of 5000 g/mol with a EO:PO ratio of 3:1) 1.5 mol/kg LiClO₄ as a function of Li doped BPO₄ (with a doping level 7 mol% Lithium) ceramic content (wt%) using Impedance Spectroscopy and Differential Scanning Calorimetry.

[1] M.J.G. Jak, Ph.D. Thesis, Delft University of Technology, 2000

[2] M.J.G. Jak, Ph.D. Thesis, Delft University of Technology, 2000

* I.J.C.M.E. Wolterink was a guest in the Department of Chemistry, Monash University at the time of this work.

AMORPHOUS NANOCOMPOSITE ELECTROLYTES: ISSUES AFFECTING CONDUCTIVITY

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Polymer electrolytes are being widely considered for electrochemical applications. [1] As an extension of this, composite electrolytes of a conducting polymer and insulating or ceramic fillers are being considered for these applications due to their improved mechanical and electrochemical properties. [2,3] Croce *et al.*'s seminal work in the area of composite electrolytes have received a large amount of attention, a nanocomposite of a polyether salt complex mixed with insulating nano-particulate fillers. Since this paper, a lot of work has been devoted to determining why the PEO₈:LiClO₄ with 10wt% TiO₂ shows a two order of magnitude increase in conductivity from the pristine polyether salt complex at room temperature. [2]

In our previous work we have used an amorphous polyether salt complex doped with similar fillers. [4,5] We have done this to remove the component of conductivity that is related to the suppression of crystallinity in PEO based electrolytes. The filler has been shown to effect ion association in the salt, modify the conformational modes in poly (methylene ethylene oxide) (PMEO) and increase T_g in the composites by several degrees. [5] The effect of the fillers on the conductivity of the composite shows a significant increase above the pure polymer electrolyte at 70°C. [4]

In this paper, we will present our recent results on the characterisation of these composite electrolytes, using new fillers and amorphous polymers, with a view towards determining a conductivity mechanism in these systems.

- [1] A. Ferry, Recent Res. Devel. Macromol. Res, 4 (1999) 79 - 93
- [2] F. Croce, G. B. Appetecchi, L. Persi, B. Scrosati, Nature 394 (1998) 456 - 458.
- [3] K.M. Nairn, A. S. Best, P.J. Newman, D.R. MacFarlane, M. Forsyth, Solid State Ionics, (1999)
- [4] A. S. Best, A. Ferry, D. R. MacFarlane, M. Forsyth, Solid State Ionics, 126 (1999) 269 - 276.
- [5] A. S. Best, J. Adebahr, P. Jacobsson, D.R. MacFarlane, M. Forsyth, in preparation for J. Chem. Phys.

PREPARATION AND ELECTROCHEMICAL CHARACTERISTICS OF THE PLASTICIZED
POLYMER ELECTROLYTE BASED ON P(VdF-co-HFP)/PVAc BLEND

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The electrochemical properties of the polymer electrolytes based on P(VdF-co-HFP)/poly(vinyl acetate)(PVAc) blend have been investigated. The polymer electrolytes were prepared by solution casting of the mixture of the blended polymer matrix and the liquid electrolyte(EC/PC/LiClO₄). The introduction of PVAc into P(VdF-co-HFP) enhanced their compatibility with the liquid electrolyte. The ionic conductivity, interfacial stability between the lithium electrode and the polymer electrolyte and the electrochemical stability window of the plasticized polymer electrolytes were characterized by varying the PVAc content in the matrix polymer. The ionic conductivity of the plasticized polymer electrolyte slightly decreased with the PVAc content. The ionic conductivity of the polymer electrolyte based on P(VdF-co-HFP)/PVAc (7/3, w/w) blend was 3.1×10^{-3} S/cm at 25°C. The interfacial stability between the lithium electrode and the polymer electrolyte was enhanced by blending PVAc with P(VdF-co-HFP). The polymer electrolyte(7/3, w/w) was electrochemically stable up to 5.0V. The performance of the unit cell was also investigated by the charge-discharge experiment.

**ZEOLITIC INORGANIC-ORGANIC POLYMER ELECTROLYTES: SYNTHESIS,
CHARACTERIZATION AND IONIC CONDUCTIVITY OF A MATERIAL BASED ON
OLIGO(ETHYLENE GLYCOL) 600, $\text{Sn}(\text{CH}_3)_2\text{Cl}_2$ and $\text{K}_4\text{Fe}(\text{CN})_6$**

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Italy

In an attempt to increase the conductivity of classic polymer electrolytes [1], it was proposed that polymer electrolytes could be modified by introducing inorganic oxides into their polymer matrix [2]. Recently, two innovative categories of metallorganic hybrids have been proposed. The first class [3] is formed by all those electrolytic products prepared by copolymerization of organic macromolecules with metal alkoxy compounds. The second class [4] includes all the materials which are named "Zeolitic Inorganic-Organic Polymer Electrolytes" (Z-IOPE). Z-IOPE are structurally constituted by inorganic negatively charged clusters bonded together by bridges of organic macromolecules. In general, the inorganic cluster site in the network is formed by complexes of two or more metal atoms.

In this report we describe the synthesis of a new Z-IOPE material of formula $[\text{Sn}_x\text{Fe}_y(\text{CN})_z(\text{CH}_3)_2\text{Cl}_v(\text{C}_2\text{nH}_{4n+2}\text{O}_{n+1})\text{K}]$. This material is based on oligo(ethylene glycol) 600, $\text{Sn}(\text{CH}_3)_2\text{Cl}_2$ and $\text{K}_4\text{Fe}(\text{CN})_6$ and was obtained via a sol-gel reaction. The TG, XPS, mid and far FT-IR studies and the analytical data allowed us to conclude that this material is a mixed inorganic-organic network where negatively charged clusters, which are formed by Fe and Sn complexes, are bonded together by PEG 600 bridges in a TGT (T= trans; G=gauche) arrangement. Scanning electron microscopy revealed a compact smooth paste morphology of the product.

Impedance spectroscopy studies showed that the material conducts ionically; its conductivity at 20°C is ca. $4.8 \times 10^{-5} \text{ Scm}^{-1}$.

[1] F.M. Gray. *Polymer Electrolytes*, RSC Material Monographs; Royal Society of Chemistry, Cambridge, UK, 1997.

[2] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, *Nature*, **394**, 456 (1998).

[3] V. Di Noto, M. Furlani, S. Lavina, *Polym. Adv. Technol.* **7**, 759 (1996); V. Münchow, V. Di Noto, E. Tondello, *Electrochim. Acta*, **00**, 00-00 (1999).

[4] V. Di Noto, *J. Mater. Res.*, **12**, 3393 (1997).

**POLY-VINYL-PYRROLIDONE IN LITHIUM
DOPED PLASTIC SALT ELECTROLYTES**

S.Pas¹, J.Golding¹, D.R.MacFarlane¹ and M.Forsyth²

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Certain lithium doped organic salts, displaying plastic crystal behaviour, have recently been shown to exhibit fast ion conduction to the order of $10^{-5} \text{ S cm}^{-1}$ at room temperature, in the solid state¹. These salts have plastic mechanical properties at room temperature, that is, applied stress may yield plastic flow. For many applications, it may be highly desirable to prevent plastic flow by reinforcing the plastic salt by means of a novel polymer in lithium doped plastic salt electrolyte.

Poly-Vinyl-Pyrrolidone (PVP) has been found to be miscible with pyrrolidinium plastic salt systems. In this work we have studied a polymer in plastic salt electrolyte, doped with lithium, based on PVP and N-methyl,N-propyl pyrrolidinium hexafluorophosphate (P_{13}PF_6). In order to understand the effect of the polymer, experimental data is analysed using: complex conductivity (ω), complex impedance, $Z(\omega)$, complex permittivity, $\epsilon(\omega)$ and complex electrical modulus, $M(\omega)$. Thermal analysis is employed to determine the phase behaviour of the system.

INFLUENCE OF THE DEGREE OF SULFONATION ON THE WATER UPTAKE AND PROTON CONDUCTIVITY FOR ACRYL AMIDE COPOLYMERS

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An important demand on proton conducting polymers for use in fuel cells is a high stability in combination with a high proton conductivity. Both dimensional and mechanical stability, as well as proton conductivity, are highly influenced by the water uptake of the polymer [1]. An increased proton conductivity and reduced dimensional stability is usually the result of a higher water content. Control of this parameter is therefore very important and can for example be gained by varying the equivalent weight (EW) of the polymer.

Poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) has in an earlier study been shown to have good hydrolytic stability combined with high proton conductivity at water contents above six water molecules per sulfonic acid group [2]. However due to the high ionic content of the AMPS homopolymer, extensive swelling in water can be a problem in fuel cell applications. In order to control the water uptake, we have synthesized copolymers of AMPS and the corresponding non-sulfonated N-*tert*-butylacrylamide (NBAA), see Figure 1 [3].

In the present study copolymers with varying EW were first swelled to equilibrium at different relative humidities. The samples were subsequently analyzed by gravimetry, calorimetry, and impedance spectroscopy. The influence of EW and humidity on the water uptake, as well as the dependence of the state of water on the conductivity, will be discussed.

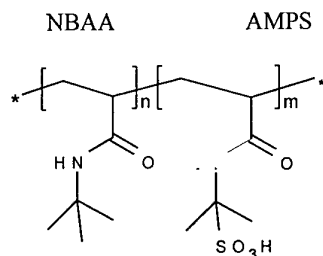


Figure 1. Poly(AMPS-co-NBAA)

The financial support from the Swedish Foundation for Strategic Environmental Research, MISTRA, is gratefully acknowledged. The work was done within the framework of the Jungner Centre.

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XPS STUDY OF LITHIUM SURFACE AFTER CONTACT WITH LITHIUM-SALT DOPED POLYMER ELECTROLYTES

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At present, lithium secondary battery using lithium metal as anode is one of the most promising secondary batteries in terms of energy density. However, the interfacial condition between lithium anode and electrolytes is one of the key factors, which are limiting the commercialization of lithium metal secondary batteries. Many researchers have been investigating the electrochemical behavior of the lithium electrode and its chemical reaction with a variety of organic and polymer electrolytes [1].

In this study, XPS analyses of lithium electrode after contact with solid polymer electrolytes were performed. New network polymer electrolytes having different number of free-end chains, prepared by photo cross-linking reaction of mixture of mono-acrylated and tri-acrylated copolymers of ethylene oxide and propylene oxide mixed with various lithium salts, have been used as polymer electrolytes.

Interfacial behavior, observed by electrochemical studies, had well showed to be affected by the number of free-chain ends. Hence, for better understanding about the charge-transfer process, lithium anode surface analysis is a complementary demand for distinguishing between the passivation layer effect at the electrode and the effect of flexible ether side chains which is expected to influence the lithium deposition/dissolution process. Type of lithium salt and effect of salt concentration in the electrolytes were also considered in this study.

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**ELECTRON TRANSFER REACTION OF POLY(ETHYLENE OXIDE)-MODIFIED AZURIN
IN POLY(ETHYLENE OXIDE) OLIGOMERS AND ORGANIC SOLVENTS**

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Poly(ethylene oxide) (PEO) is a polymer solvent for the electrochemical redox reaction. PEO is also well-known as the most popular material for the protein modification. We have extensively studied the electrochemical response of a various kind of PEO-modified heme proteins in PEO oligomers [1]. In this study, we apply this strategy to azurin (Az) which is one of copper-containing electron transfer proteins. PEO₂₀₀₀ (av. MW: 2000)-modified Az (PEO₂₀₀₀-Az) was synthesized according to the previous method reported on the modification of the heme proteins [2]. The similarity between the UV-vis, CD, and ESR spectra of PEO₂₀₀₀-Az and the native ones in the buffer solution suggests that PEO-modification doesn't cause any structural change at the copper site. PEO₂₀₀₀-Az becomes soluble in PEO₂₀₀ (av. MW: 200). These spectroscopic methods also show that PEO₂₀₀₀-Az is stable even in PEO₂₀₀. The investigation of the electron transfer reaction of PEO₂₀₀₀-Az in PEO₂₀₀ is in progress.

Moreover, PEO₂₀₀₀-Az becomes soluble in the various organic solvents. When we use benzene as the solvent, the direct electrochemical response of PEO₂₀₀₀-Az has been observed at the PEO-thiolate-modified gold electrode.

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POLYPYRROLE-BASED BIOSENSOR FOR THE DETERMINATION OF CHOLESTEROL

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Cholesterol is a type of fat which has a large molecule with a complex nucleus and a waxy texture. The majority of cholesterol is produced by the body according to its needs, but it is also absorbed from the ingestion of food with animal sources, such as eggs, milk, cream and butter. A certain level of cholesterol is essential for the body to be able to perform several functions. However, excessive levels of cholesterol in the body can contribute to coronary heart disease and has also been linked with other diseases, such as arteriosclerosis, myocardial infarction and lipid metabolism dysfunction. Hence, there is often a need for individuals who are genetically pre-disposed to these diseases to regularly monitor cholesterol concentrations. The availability of a convenient and reliable method for measuring cholesterol in various samples without any pre-treatment is of paramount importance to this and other clinical diagnosis.

In this paper, we will describe an electrochemical approach employed for the development of a polypyrrole-based cholesterol biosensor, involving the entrapment of an enzyme, cholesterol oxidase, by galvanostatic polymerisation of pyrrole. The use of this device for the determination cholesterol will be discussed. Various instrumental and solution parameters that are important in improving the reliability of the biosensor will also be discussed. Future use of the biosensor to determine levels of cholesterol in real samples will be outlined.

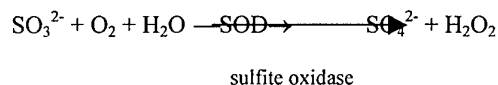
FABRICATION OF A POLYPYRROLE-DEXTRAN-SULFITE OXIDASE BIOSENSOR

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The reliable determination of sulfite in foods and beverages is of utmost importance for regulatory purposes and for on-going evaluation of dietary exposure because the ingestion of foods containing high levels of sulfites can cause abdominal pain, diarrhea, reaction with cellular components, toxicity and death. Sulfites are preservatives that are used primarily as antioxidants in the food and beverage industry.

To date, most of the reported methods for the detection of sulfite in food and beverages are complicated, time consuming and not practical for numerous routine determinations. One exceptions to this criticism is the enzymatic method, which involves the following catalytic reaction:



The approach we have adopted in our laboratories for detection of sulfites based on this reaction involves the simultaneous formation of a conducting polypyrrole support and the entrapment of SOD by electroimmobilisation. In effect the fabrication of the biosensor involves concurrent galvanostatic polymerization of pyrrole and entrapment of SOD. This is a more direct and rapid approach for the detection of sulfite than other enzymatic methods. The potential advantages of using this biosensor are rapid and specific quantification, without the need for sample preparation.

In this paper, a more recent approach developed for synthesising a composite polypyrrole-dextran film and its use for fabrication of a robust sulfite biosensor will be described. Various factors influencing the optimum performance of the biosensor, as well as its stability, sensitivity and response time of the biosensor will be discussed. Also, some applications of the biosensor to real samples will be highlighted.

CONTROL OF IONIC CONDUCTIVITY USING BORON COMPOUNDS

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Reduction of ion pairing of electrolyte salts is a useful method for raising ionic conductivity of organic electrolyte solutions. At present, most of aprotic solvents used in organic electrolyte solutions mainly coordinate to cations. However, since enhancement of the ionic conductivity and the lithium ionic transference number is preferable for the electrolytes of lithium batteries, the coordination of solvents to anions is more favorable than that to cations. In this study, in order to increase both cationic mobility and cationic transference number, we have synthesized boron compounds that selectively coordinate to anions. The addition of the boron compounds to organic electrolyte solutions leads to the result that dissociation of electrolyte salts is promoted and anion mobility is restricted. When the boron compounds are added to such solvents as 1,2-dimethoxyethane (DME) and γ -butyrolactone (GBL) containing various lithium salts, the ionic conductivities of these solutions considerably improve as compared to those without the boron compounds. Furthermore, we will discuss the effect of the boron compounds in polymer gel electrolytes.

NMR AND ION CONDUCTIVITY STUDIES OF A ETHYLENEOXIDE-PROPYLENEOXIDE
PRECURSER MONOMER DOPED BY $\text{LiN}(\text{SO}_2\text{CF}_3)_2$

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Since the diffusion phenomena of the ions in the cross-linked polymers were very complicated, the measurements of the T_1 , T_2 , and the self diffusion coefficients of the ^1H - ^{19}F - and ^7Li - NMR were made for the precursor monomer. The monomer structure is a glycerol derivative of ethylene oxide (EO) and propylene oxide (PO), the ratio being 8:2 and terminated by the methyl group. The molecular weight is about 8,000. The sample is liquid at the room temperature. We measured the NMR spectra for the pure solvent and the solution electrolyte doped by $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ with the mole ratio 20:1 by oxygen of the solvent and the Li.

The T_1 and T_2 (spin-echo) relaxation curves were all analysed by a single exponential for the lithium ion, anion, and solvent. The temperature dependent T_1 plots of the polymer and the lithium showed the minimum and the relaxation mechanism can be assumed by the dipole-dipole and the quadrupolar interactions for the ^1H and ^7Li NMR, respectively. The calculated correlation times indicate that the lithium motion is slower than the polymer motion. At the same temperature the correlation time of the pure solvent is faster than that of the electrolyte solvent.

The apparent self diffusion coefficients of the lithium, the anion and the solvent can be analysed as a freely diffusing particle but depend on the measuring parameter Δ . This trend becomes pronounced as the temperature decreases. Here we propose the model of the diffusion in the liquid system.

MICROPOROUS POLYMER ELECTROLYTE MEMBRANES

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One of the main challenges in the development of new electrolytes is to prepare materials that combine high dimensional stability with sufficient ionic conductivity. The conductivity of a polymer electrolyte is commonly improved by adding a plasticizer to the system. Unfortunately, this often impairs the mechanical stability of the system. One strategy to overcome the problem is to incorporate the conductive phase in a mechanically stable three-dimensional matrix. [1]

In the present paper we report on heterogeneous solid polymer electrolyte membranes based on a continuous network of crosslinked poly (ethylene glycol) monomethyl ether monomethacrylate macromonomers incorporated in a microporous network of poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP). In this material the conductive phase consists of the crosslinked macromonomer. The matrix material PVDF-co-HFP has good physical and mechanical properties, and is partly miscible with short poly (ethylene oxide) chains, such as the macromonomers. [2]

Mixtures of PVDF-co-HFP, macromonomer, and crosslinker were UV-irradiated to induce polymerization. In connection with the polymerization, a microphase separation occurred. Solid polymer electrolytes were subsequently obtained by doping the polymer membranes with LiPF_6 . The influence of the salt concentration and the composition on the morphology and conductivity was studied.

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Acknowledgement:

The financial support from the Nordic Energy Research Program is gratefully acknowledged.

EFFECT OF HIGH PRESSURE ON THE ELECTRICAL CONDUCTIVITY OF ION CONDUCTING POLYMERS

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The variation of the electrical conductivity with pressure at various temperatures has been determined for ion conducting polymers such as poly(propylene glycol) and poly(ethylene glycol) containing lithium or sodium salts. The electrical conductivity is inferred from complex impedance measurements over the frequency range of 1 mHz to 1 MHz. The complex impedance measurements were carried out at pressures up to 0.3 GPa and at temperatures from 200 to 400K. The usual decrease of the pressure derivative of the electrical conductivity (and hence activation volume) with temperature is observed. It is shown that all results can be explained via a generalized Vogel equation that has recently been extended to include the effects of pressure. In fact, the general features of the experimental results for the pressure dependence of the electrical conductivity can be predicted from the zero pressure results (variation of the electrical conductivity with temperature) using no adjustable parameters. All that are required are the compressibility and the variation of the glass transition with pressure. Other applications of the theory are also discussed.

COMPLEX IMPEDANCE STUDIES OF S-SEBS BLOCK
POLYMER PROTON-CONDUCTING MEMBRANES

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Water uptake, swelling, ¹H pulsed gradient spin-echo nuclear magnetic resonance (NMR) and variable temperature and pressure complex impedance/electrical conductivity studies have been carried out on sulfonated styrene /ethylene-butylene /styrene (S-SEBS) triblock polymer proton conducting membrane. All of the data show different characteristics above and below about 10 wt-% water. For example, the diffusion coefficients, D from NMR and D_G calculated from conductivity data (which are the same to within experimental uncertainty), show different dependence on water above and below about 10 wt-%. At high water content, the properties of S-SEBS are similar to those for Nafion 117, proton transport being similar to that in bulk water. For low water contents, however, the materials are different. For low water content S-SEBS, the variation of the conductivity with temperature is Arrhenius while that for Nafion 117 is not. The variation of the electrical conductivity with pressure gives rise to activation volumes on the order of 14 cm³/mol while those for Nafion 117 are about four times larger. These results indicate that proton transport in low water content S-SEBS occurs via a thermally activated process (ion motion via energy barriers) that is consistent with the more rigid side chains in that material.

STUDY OF ELECTROCHEMICAL SUPERCAPACITORS USING
POLYURETHANE ELECTROLYTES / CARBON BLACK COMPOSITES

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Electrochemical capacitors are electrical devices that display characteristics between conventional capacitors and rechargeable batteries. These devices have been considered for their use in integrated storage systems for electrical vehicles. Among the main technologies utilized to build polymer-based supercapacitors, the dispersion technique of Carbon Black (CB) in a solid polymer electrolytes (PE) matrix has been chosen to develop polarizable electrodes. We report here preliminary results concerning the study of a flexible solid state system, using PE and CB materials, based on the use of composite electrodes and large-area current collectors. The optimal PE material was obtained by the dissolution of 18 wt% LiClO₄ in a synthetic thermoplastic polyurethane of poly(tetramethylene glycol)-*co*-poly(ethylene glycol). The performances of the as-prepared capacitors were characterized by a variety of electrochemical techniques including impedance spectroscopy, cyclic voltammetry, galvanostatic charge-discharge methods, and long term cycling tests. All the studies were performed under ambient conditions with no special handling cares. The electrical device prepared with 20 wt% CB composite electrodes exhibited a maximum capacity of 4 F cm⁻³ under 2V providing an energy density of 2 Wh L⁻¹, with a peak power of about 120 W L⁻¹. This selected device configuration presented promising electrical and mechanical properties with an electrochemical stability exceeding 2V; further work is in progress to increase the percolation limit and the value of capacitance.

MEASUREMENT OF ELECTROCHEMICAL STABILITY OF GEL ELECTROLYTES FOR LITHIUM BATTERIES

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Gel electrolytes are currently employed, instead of the liquid variety, in consumer rechargeable lithium-ion batteries. An advantage of gels is their safety aspects, such as containing components that are less volatile and have a better chemical stability. In the design and synthesis of new gel electrolytes for use in lithium-ion batteries, one objective is to achieve improved stability in the region near the electrodes. The gel has to be able to withstand both extreme oxidising and reducing environments without reacting or degrading. Electrochemical methods, such as cyclic voltammetry, have been widely used to quantitatively investigate the electrochemical stability of such electrolytes. An investigation of the methods reveals different results, depending on the choice of experimental conditions and method, which are influenced by both reaction thermodynamics and kinetics [1]. In this study, electrochemical methods were employed to characterise the electrochemical stability of lithium battery gel electrolytes. The goal was to find a suitable method and to investigate the influence of the experimental conditions. Gel electrolytes, based on PMMA or acrylic graft co-polymers with EC/g-BL solvents and LiPF₆ or LiTFSI salts, were tested with several electrode materials, such as stainless steel, platinum and carbon. Different types of electrochemical experiments were carried out, e.g. cyclic voltammetry and chronoamperometry. In addition, the stabilities of some of the electrolytes were tested by cycling battery cells, that were made of graphite and LiMn₂O₄ electrodes and the electrolyte of interest. The results showed that the experimental conditions are important to consider when measuring electrochemical stability, and that both the kinetics and thermodynamics of the degradation reactions play significant roles.

The financial support from the Swedish Foundation for Strategic Environmental Research, MISTRA, is gratefully acknowledged. The work was done within the framework of the Jungner Centre.

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POLY(PROPYLENE OXIDE)/ SULFONAMIDE
SALT HYBRIDS AS NEW ION CONDUCTIVE POLYMERS

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Poly(propylene oxide) (PPO) is a typical polyether having low glass transition temperature (T_g). However, PPO generally exhibits low ionic conductivity because of poor ability to produce carrier ions. In this study, we synthesized new PPO having high dissociation sulfonamide (SA) salt part on the chain ends (PPO/SA salt hybrid) and evaluated the structural effect on the ionic conductivity.

Linear and branched PPO/SA salt hybrids were obtained by the reaction of linear or triol type PPO oligomers (PPO-NH₂, PPO-(NH₂)₂, PPO-(NH₂)₃) and a series of alkyl sulfonyl chlorides (R-SO₂Cl; R=CF₃, CH₃ or C₆H₅). Chemically cross-linked hybrids were synthesized by the interfacial polycondensation reaction with naphthalene-1,3,6-trisulfonyl chloride and PPO-(NH₂)₂ under the presence of LiOH. All the sulfonamide acids thus obtained were neutralized with LiOH.

All lithium salt hybrids were revealed to be amorphous with the DSC measurement. Linear and branched hybrids were viscous liquid and kept low T_g below -60 °C. The hybrid salts having trifluoromethyl group neighboring SA group showed high ionic conductivity above 10⁻⁶ Scm⁻¹ at room temperature. The VTF plot suggested that the strong electron withdrawing effect of the trifluoromethyl group improved the dissociation degree of the sulfonamide group. On the other hand, the cross-linked hybrid was obtained as a rubbery solid. However, the ionic conductivity was extremely low. The cross-linked hybrid showed excellent compatibility with low molecular weight hybrids, and these mixtures showed high ionic conductivity above 10⁻⁶ Scm⁻¹ at room temperature in solid state.

PREPARATION AND CHARACTERIZATION OF A NOVEL LITHIUM SALT BASED POLYMER ELECTROLYTE

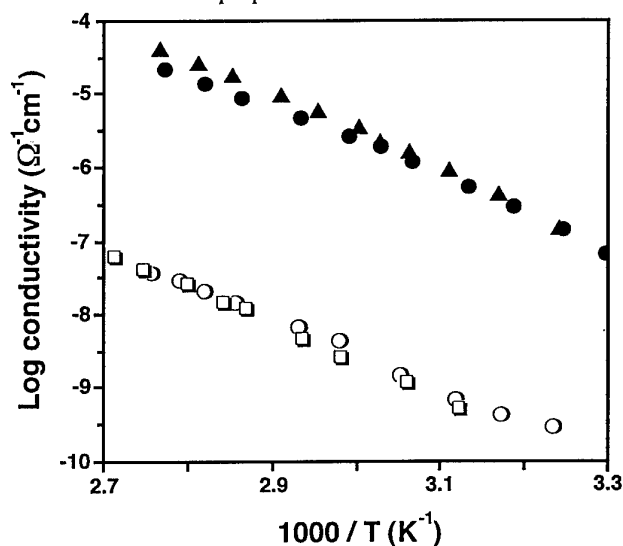
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The results of a preliminary investigation of two new solvent-free polymer electrolytes based on a novel polymer host with lithium trifluoromethansulphonate (triflate) and lithium perchlorate, are described in this presentation. Electrolytes with a range of lithium salt compositions between $n = 3$ and 90 (where n represents the molar ratio of polymer units per lithium ion) were prepared by dissolution of salt and polymer to form a homogeneous solution in anhydrous solvent. Thin films of electrolyte were produced by slow evaporation of these solutions under a dry argon atmosphere.

The solvent-free electrolyte films produced were characterised by measurements of total ionic conductivity, differential scanning calorimetry and thermogravimetry. The triflate-based electrolyte showed superior thermal stability but with lower ionic conductivity than that of perchlorate-based electrolyte samples with similar salt concentration. The highest conductivity (approximately $5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$) was found at about 95°C with the perchlorate-based electrolyte composition of $n = 3.5$. Electrolytes with this composition were obtained as very transparent, completely amorphous films with excellent mechanical properties.



Range of conductivities of the electrolytes studied

added salt

Li ClO₄ $n = 73$ ○, 3.5 ▲

Li CF₃SO₃ $n = 55$ □, 9 ●

**BINDING ISOTHERMS CALCULATED FOR INTERACTION OF Cu^{2+} and Ca^{2+} IONS WITH
DNA ON ITS COMPACTISATION IN TERMS OF STATISTICAL SUM OF
MACROMOLECULE**

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In our previous works [1, 2] we have shown that under the action of Cu^{2+} and Ca^{2+} ions DNA is able to transit into the compact state in aqueous solution at 29°C. DNA compactisation may be both of intra- and intermolecular character. This process is highly cooperative. DNA in the compact state remains in B-conformation limits [1, 2].

In the presence of alcohol DNA condensation occurs at a rather lower concentration of Me^{2+} ions than that of aqueous solution. In this case binding constants and cooperativity of the metal ion binding rise and binding isotherms (i.e. dependences of the binding degree r on the concentration of free metal ions C_f) take a nonmonotonous S-like character with metastable and nonstable parts characterised with the reverse dependence of r on C_f . Such isotherms for a stable process may be replaced with a dependence with a jump along r , that evidences a phase transition. Thus, the DNA transition into the compact state under the Cu^{2+} and Ca^{2+} ions action in aqueous-ethanol solutions may take the character of a phase transition [2]. But when calculating binding isotherms in [2], we did not take into account the distribution of values along the assembly of DNA molecules. To obtain the more sequential thermodynamic description for the system of ions interacting with the biopolymers, in the present work we carried out calculations in terms of the macromolecule statistical sum. In this case binding isotherms are not nonmonotonous with any values of binding constants and cooperativity parameters. This is connected with the fact that the use of accurate expression for the statistical sum leads to the automatic fulfilment of all the thermodynamic inequalities.

Thus, on the coil - globule transition single DNA molecules may undergo the first-kind phase transition while the transition of the assembly of DNA molecules is of sigma-like character typical of the cooperative and continuous transition.

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OPTICAL TRANSPARENT ION CONDUCTING MODIFIED POLYMETHYLMETACRYLATE POLYMER

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We have shown an opportunity of management for electrical conductivity of polymethylmetacrylate (PMMA) organic glass with preservation of its transparency in visible area of a spectrum for the first time. More detailed research has shown presence in PMMA modified by ions of alkaline metals of the ionic conductivity. The correlation for values of electrical conductivity and cation radius specifies presence in system "PMMA - salt of metal ion" the dipole interaction. The sample which was modified by potassium ions has the maximal meaning electric conductivity (order 10^{-6} Sm/m - without the solvent, including without sorption water). Potassium has greatest potential of ionisation in a set Li - Na - K. The ionic conductivity grows more than on 4 range about in case of introduction in this concrete system low molecular of the solvents with high dielectric permeability. For example, electrical conductivity of a polymeric material at 298 grad K raises up to 10^{-2} and 10^{-3} Sm/m at introduction formamide or water (5 % weight) accordingly.

The settlement meanings of diffusion factor and mobility of ions in polymeric electrolyte (PE) are equal $7 \cdot 10^{-8} \text{ m}^2/\text{Om} \cdot \text{mol}$ and $2 \cdot 10^{-9} \text{ m}^2/\text{s}$ accordingly at the contents of potassium ions 6 mol/kg at 298 grad K. Weight of potassium allocated on platinum electrodes at electrolyse of PE was measured: the output on a potassium is about 30 % from theoretical.

This PE is used as a sensitive element of the gauge of humidity, the membrane voltamperometric sensor of control, ion a selective electrode. Modified PMMA is optical transparent in visible area of a spectrum. This property can allow for use it in electroluminescent flat indicators.

SANS STUDY ON INTERACTION OF MICELLAR AGGREGATES
AND MICRO-EMULSIONS OF POLYELECTROLYTE COPOLYMERS

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Diblock polyelectrolyte copolymers styrene-b-sodium acrylate (PS-PANa) were studied in aqueous solution with small angle neutron scattering (SANS). Spherical micellar aggregates were found to self-assemble with polydispersity of 10%. The aggregation number remains roughly constant in a range of polymer concentration. The polyelectrolyte micelle hairs, consisting of the PANa block, were found to be extremely stretched, due to intra-micellar charge repulsion, thus making the outer shell rigid. The interaction between micelles is prominent even at 0.1% polymer concentration. To describe the interaction, the inter-micellar structure factor can be best fit using a hard sphere/square well potential with Sharma-Sharma mean spherical approximation. We propose that the hard sphere interaction is due to the rigidity of the outer shell, while the attraction is due to an induced dipole dispersion interaction between the monomers. Introducing a third phase, toluene, into the micelle dispersion, monodispersed micro-emulsions were found to form by core-swelling with no reorganization of the micellar aggregates. Increasing the toluene to a content higher than that of copolymer, polydispersed spherical emulsions of 1 to 100 micron size were observed.

PVDF-BASED POROUS POLYMER ELECTROLYTES

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The most recent research activity in the field of solid polymer electrolytes has shown that good results can be obtained by means of porous polymer matrices embedded (swollen!?) by organic solutions containing lithium salts (1, 2). By using PVdF homopolymer it is possible to obtain conductivities as high as $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature, while outstanding mechanical properties are maintained.

In this paper we will discuss the preparation and the physico-chemical characterization of solid polymer electrolytes based on porous films having up to 70% of porosity. Attention will be chiefly devoted on the phase structure deriving from the film activation with the electrolyte solution. The picture is emerging of multiphase systems in which the majority of the solution is trapped into the cavities (0.5-1 μm range), while a non-negligible fraction of the salt-solvent mixture swells the amorphous strands of the polymer, as expected on the basis of the classical theory (3).

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PREPARATION OF POLY(PROPYLENE CARBONATE) BASED
GELLED POLYMER ELECTROLYTES FRO LITHIUM POLYMER BATTERY

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New plasticized ionic conducting polymer membrane was prepared with poly (propylene carbonate methacrylate) (PCMA) and oxymethyl linked poly(ethylene oxide) (mPEO) by using UV and heat cross linking techniques. Poly(propylene carbonate methacrylate) and oxymethyl linked poly(ethylene oxide) were synthesized and verified structures with NMR and IR spectroscopy. The prepared ionic conducting membrane was analyzed with various electrochemical tools and applied to lithium polymer battery. The PCMA and mPEO based polymer membrane was prepared with addition of 50wt% of 1M LiPF_6 in ethylene carbonate (EC)/propylene carbonate(PC) mixture into a PCMA and mPEO polymer matrix. The EC/PC liquid electrolyte is working as a plasticizer which reduce highly crystalline structure of PCMA polymer matrix. This plasticized PCA membrane shows excellent mechanical and electrochemical stability in wide ranges of electropotential windows at 0~5.0V. The obtained PCMA membrane shows ionic conductivity as high as 6×10^{-4} S/cm at the ambient temperature. In terms of ionic conductivity on polymer membrane, the effects of plasticizer in crystalline polymer have been proved through many previously published papers. In addition to increasing ion conductivity by plasticizing effects of PCMA, the propylene carbonate group on PCMA polymer which keep high dielectric constant of polymer matrix itself. In this paper, the effects of plasticizer in the PCMA and mPEO matrix will study and will discuss about the applications of lithium polymer battery with this PCMA and mPEO ionic conducting polymer electrolyte.

**A DENSITY FUNCTIONAL STUDY OF THE
BIS[TRI(FLUOROMETHANE)SULFONYL]AMIDE (TFSA⁻) BASED SALTS USING A TFSA⁻
Li⁺ MODEL**

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Molten organic salts have been of substantial interest due to their low melting points and stability at or near room temperature. The anions TFSA⁻, (CF₃SO₂)₂N⁻, and its relatives CF₃SO₃⁻, CH₃SO₃⁻ and (CH₃SO₂)₂N⁻, when combined with an appropriate cation, produce such stable, low temperature melts, which may have applications in solar cells, Li batteries and as benign solvents in synthesis. These anions are also of interest as their lithium salts in solid polymer electrolytes.

The recent crystal structure elucidation of TFSA⁻ [1] has prompted the need to further understand the nature of such systems. A study of TFSA⁻Li⁺ as a model for TFSA⁻ based ionic liquids is in progress.

We aim to identify the key characteristic structural parameters of the anion and obtain an accurate potential map of the TFSA⁻Li⁺ pair using density functional theory (DFT) combined with pseudospectral methods.

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CURRENT R&D AT THE ÅNGSTRÖM ADVANCED BATTERY CENTRE

S. Abbrent, A.M. Andersson, A. Bishop, H. Björk, K. Edström,
T. Eriksson, P. Eyob, L. Fransson, T. Gustafsson, M. Herstedt,
J. Höwing, S. Nordlinder, J. Lindgren, J. Tegenfeldt and J. O. Thomas

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Uppsala University has a more than 15-year tradition of lithium-polymer and lithium-ion/polymer battery research. Initially, our interests lay entirely within the area of materials characterisation; first of polymer electrolytes, and later of anode and cathode insertion materials. Our focus has subsequently broadened to encompass such "battery engineering" aspects as cyclability, shelf-life, elevated-temperature performance and safety. The scope of our current activities thus spans from synthesis and characterisation of novel battery materials, through optimisation of their performance in composite electrodes, to their ultimate incorporation into complete cell prototypes. We also perform extensive molecular dynamics (MD) simulation and band-structure calculations in support of our experimental work.

Structural characterisation techniques include *in situ* XRD and neutron diffraction at ambient and elevated temperatures. Electrochemical interface and surface phenomena are probed using XPS, SEM and BET techniques. Vibrational spectroscopic techniques (FT-IR and Raman) are used both for structural and surface studies. Cell performance is monitored using Digatron and MacPile cycling devices and AC impedance. Cell reactions are studied using DSC and cyclic voltammetry.

On the *cathode* side of the cell, LiMn_2O_4 , LiCoO_2 , LiFePO_4 , $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and V_6O_{13} are among the materials we study. *Anode* materials of interest include synthetic and natural graphites, tin-based metal alloys (e.g. Cu_6Sn_5 , in collaboration with Argonne National Laboratory) and glasses (in collaboration with CTH, Gothenberg). We study liquid and polymer electrolytes, incorporating both plasticised polymer electrolytes and molten salts. Some of these materials are also relevant to fuel-cell activities.

Our poster will present an overview of some of the on-going research projects at the Ångström Advanced Battery Centre.

Funding sources: EU (3rd and 4th Frameworks); MISTRA; NFR; TFR; NERP; STEM; and The Wallenberg Foundation.

TESTING POLYMER MEMBRANES FOR AN ELECTROWINNING PROCESS

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Conventional zinc electrowinning is carried out in single compartment cells typically at a cell voltage of 3.3 V, and a coulombic efficiency of about 90%. The overall process converts a concentrated neutral zinc sulfate solution to a sulfuric acid solution containing residual zinc sulfate. Zinc and some by-product hydrogen are produced at the cathode. At the anode, the main reaction is oxygen evolution, but the impurities, manganese(II) and chloride may be oxidised, significantly raising the redox potential of the solution. Acid is produced at the anode, and a small amount is consumed at the cathode.

The cathode process is very sensitive to zinc and acid concentrations, especially if certain impurities are present above particular trace levels [1]. Several conceptual cell arrangements for increasing the intensity of electrowinning exist [2-6]. In some cases, the sensitivity to acid is increased [5]. This provides one justification for the study of polymer membranes for incorporation in advanced cell designs. Other possible benefits of a membrane are outlined.

Preliminary tests indicated that some commercial anion exchange membranes had acid transference properties appropriate for development of a membrane cell process. A range of laboratory techniques was then developed and used to measure several pertinent properties of modified anion exchange membranes, as well as other separators. High current densities, as envisaged for spouted bed electrowinning of zinc [6], were investigated. This paper describes these techniques and gives the range of results encountered for key parameters.

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ELECTROLYTES BASED ON AGGREGATING COMBLIKE POLY(ETHYLENE OXIDE-CO-PROPYLENE OXIDE)

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Aggregating polymer systems capable of facilitating ion conduction can successfully be employed as solid state electrolytes [1,2]. Comblike copolymers, characterized by having a large number of oligomeric grafts attached to a polymeric backbone, may be designed to form the building blocks in such systems. Aggregating copolymers can for example be achieved by incorporating chain end segments with a degree of polarity dissimilar to that of the grafts. These modified comblike copolymers may form continuous networks by interpolymer aggregation through phase separation of the chain end segments.

In the present study, comblike copolymers (Fig. 1) were prepared by using a poly(*p*-hydroxystyrene) backbone as a multifunctional initiator for anionic graft copolymerization of ethylene oxide (EO) and propylene oxide (PO). Because EO is more reactive than PO, the former will have a higher rate of consumption [3]. The grafts thus had a 'tapered' microstructure, that is, the composition changed gradually along the chain. The microstructure of the grafts can be expected to greatly influence the phase behavior and ion conductivity of the polymers. Comblike copolymers having both 'single tapered' and 'double tapered' grafts were prepared. In the final step, hexadecanoyl units were attached to the ends of the grafts through esterification. The preparation, phase behavior, and ion conductivity of electrolytes based on these polymers will be discussed in the presentation.

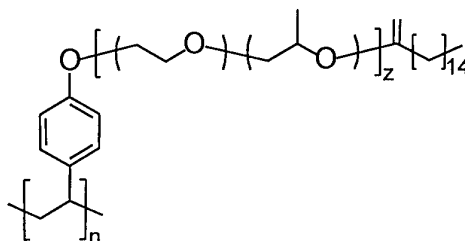


Fig. 1 Combshaped poly(EO-co-PO) with hexadecanoyl chain ends.

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NMR AND IONIC CONDUCTIVITY STUDY OF NON-AQUEOUS PROTON
GEL ELECTROLYTES BASED ON POLY(VINYLDENE FLUORIDE) AND H_3PO_4

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Proton conducting gel electrolytes based on a network of poly(vinylidene fluoride) containing perdeuterated H_3PO_4 have been synthesized using propylene carbonate (PC), dimethylformamide (DMF), and dimethylamide (DMA) as entrapped solvents. These systems have ionic conductivities as high as 10^{-3} Scm^{-1} at ambient temperatures. The operating range of these electrolytes is from 220 to 370 K. In an attempt to understand their structure and dynamic properties, we report measurements of self-diffusion coefficients (D) of mobile species for these materials at room temperature, using ^1H ($I=1/2$), ^2H ($I=1$) and ^{31}P ($I=1/2$) pulsed field-gradient Hahn spin-echo techniques. Thus all diffusing species, solvent/plasticizer (^1H), acid hydrogen (^2H), and phosphates (^{31}P) were measured separately. The diffusion data conclusively show that deuterons diffuse faster than the phosphorus carrying species. Also ^{31}P diffusion coefficients of the different phosphate species present are, as expected, dependent on the size of the moving species. Similar measurements were performed on their H_3PO_4 solution analogues to examine the role of the gel network, if any, in the conduction process. The ion transport mechanisms in these gels are discussed.

PLATINUM ELECTRODEPOSITION FOR POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

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The electrodeposition of platinum into Polymer Electrolyte Membrane Fuel Cell (PEMFC) electrodes may enable an increased utilisation of platinum compared with conventional chemically-prepared platinum catalysts. With an increased platinum utilisation higher current densities could be attained, resulting in a reduction in the PEMFC weight and volume.

Platinum-supported-on-carbon (Pt/C) is conventionally prepared from a sodium platinum sulfite compound, $\text{Na}_6\text{Pt}(\text{SO}_3)_4$. In this 'sulfite route', unstable platinum colloids are chemically prepared and then precipitated onto the carbon support [1]. The Pt/C prepared by this method is more suited for use with liquid electrolytes, where all of the platinum particles may be accessed. In a PEMFC however, the polymer electrolyte (eg. Nafion) is less mobile and may have poor contact with the platinum, hence reducing the amount of platinum able to participate in fuel cell reactions. An electrodeposition method may allow greater control over the platinum placement at the electroactive sites, ie. sites having both ionic and electronic contact [2,3].

Two electrodeposition methods are described in this work. In one case, the novel electrochemistry of the platinum salt, $\text{Na}_6\text{Pt}(\text{SO}_3)_4$, has been investigated. It was found that platinum may be electrodeposited onto a carbon substrate from a solution of this salt. During the deposition reaction, a sulfur species is produced which is believed to poison the deposited platinum. This poisoning reaction may enable the preparation of nanosized platinum particles as required for catalyst applications in fuel cells. In the second case, the platinum salt, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$, was ion-exchanged into a Nafion-impregnated electrode and subsequently electroreduced to form the active platinum catalyst.

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NMR, DSC AND CONDUCTIVITY STUDY OF HEC/POLYETHER BASED POLYMER ELECTROLYTES

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A. Gandini³, J.-F. LeNest³

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Polymer electrolytes based on hydroxyethylcellulose (HEC) / polyether were investigated by NMR, DSC and AC conductivity. Poly(ethylene oxide) based di-isocyanate (DPEO) was synthesized [1] and the condensation reactions with HEC samples were performed under nitrogen atmosphere from dry dimethylacetamide (DMAc) solution, using traces of dibutyltin dilaurate as catalyst. The transparent film of HEC/DPEO/LiClO₄, ([O/Li]=12) show a glass transition temperature $T_g = 253$ K and ionic conductivity of $\approx 10^{-5}$ S/cm at room temperature. Proton (¹H) and ⁷Li NMR line shapes and spin-lattice relaxation times (T_1) were measured at the Larmor frequency of 36 MHz (¹H) and 155.4 MHz (⁷Li) in the temperature range of 140 - 350 K. Only one ¹H absorption band in the proton spectra, and ¹H and ⁷Li exponential relaxation were observed throughout all the temperature range investigated. Motional narrowing of the ¹H NMR line was observed to occur near T_g , reflecting the correlation between the polymer segmental motion and the ionic mobility. The temperature dependence of the ¹H and the ⁷Li T_1^{-1} of HEC/DPEO/LiClO₄ shown single relaxation rates maxima and the activation energy obtained from the NMR data is $E \approx 0.24$ eV. The correlation times for the Li⁺ motion calculated from the NMR data indicate that the relative mobility of the cation in this sample is comparable to those observed in PEO-Li based polymer electrolytes, the former showing a predominance of amorphous phase. Our results indicate that HEC/DPEO/LiClO₄ are a suitable solid polymer electrolyte for several applications such as sensors, solid state batteries and electrochromic devices.

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POSTER SESSION II

Wednesday 9th August
8.00pm - 9.30pm

A PROTON CONDUCTOR BASED ON SILICOTUNGSTIC ACID

J. Sun*, L. Jordan*, D. R. MacFarlane[#] and M. Forsyth*

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Conductivity of a single crystal STA (28H₂O) has previously been reported^[1] as high as $2.7 \times 10^{-2} \text{ S.cm}^{-1}$ at room temperature, which suggested that STA could be potentially used in solid electrolyte compositions with a sufficient conductivity for low temperature fuel cell application. Kucernak et al ^[2] studied an STA aqueous solution as an electrolyte in a direct methanol fuel cell, and they investigated the enhancement in electrocatalytic activity towards methanol oxidation due to presence of STA in electrolyte solution. STA (with 24H₂O) was used in an anolyte composition with H₃PO₄ and PtO₂ for chemically regenerable redox fuel cells by Kummer et al ^[3]. Despite its potential, STA has still not been extensively investigated as a proton conductor component of a solid electrolyte. In this work, it was found that STA could be mixed with phosphoric acid (H₃PO₄, 85%) to make a viscous paste material with high conductivity ($10^{-2} \text{ S.cm}^{-1}$ at room temperature), and the STA/H₃PO₄ paste samples were quite stable at 80 °C in the atmosphere, and at 100 °C under constant humidity over 10 days. The stability of the paste samples have been investigated under different conditions, and it was found to be affected by several factors, including temperature, paste composition, and environment humidity. Furthermore, the incorporation of STA in a polymer matrix such as poly(benzimidazole) has been explored and also showed promising results under humid conditions.

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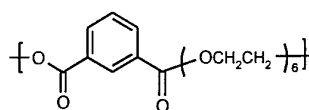
STUDIES IN LIQUID CRYSTALLINE POLYMER ELECTROLYTES

L. J. Barlow, C. T. Imrie and M. D. Ingram

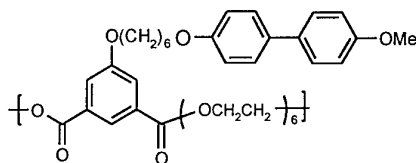
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As part of a continuing investigation into the phenomenon of decoupled ion transport in polymer electrolytes [1] we are currently examining the behaviour of the following systems:

- 1) A series of polymer-salt complexes based on "0G6" and LiCF_3SO_3 , where 0G6 is:



- 2) A series of polymer-salt complexes as for (1) using "MeOC6G6" and LiCF_3SO_3 , where MeOC6G6 is:



Techniques used include ac impedance spectroscopy, DSC, DMTA, TG-MS and polarised light microscopy.

[1] C.T. Imrie, M.D. Ingram and G. S. McHattie, *Adv. Mater.* 11 (1999) 832-834.

NOVEL PROTON CONDUCTING POLYMER ELECTROLYTES FOR ELECTROCHROMIC SYSTEMS

Zbigniew Florjanczyk, Ewa Zygadlo-Monikowska, Anna Wojda and Wladyslaw Wieczorek

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Novel proton conducting gel electrolytes for operation in electrochromic devices have been elaborated. As it is known, proton conducting systems presently used, in general operate in an aqueous medium (fuel cells, sensors). Due to the quick corrosion of the electrodes, they cannot be applied in electrochromic devices. Therefore, lithium salts in an organic medium or solutions of acids in organic solvents are being applied in most of them. Phosphoric acid esters, which are characterized by higher dissociation constants than that of phosphoric acid, have been used in the work presented as a source of protons. The phosphoric acid esters were obtained from the reaction of phosphoric acid with epoxide compounds such as ethylene oxide or propylene oxide. Polymeric matrices in the gels studied were obtained in the copolymerization or terpolymerization of glycidyl methacrylate with various acrylic monomers (methyl methacrylate, acrylic acid, acrylonitrile) utilizing reactions involving epoxide groups in the crosslinking process. The gel electrolytes thus obtained are characterized by high ionic conductivity of the order of $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at room temperature and $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 50°C , only slightly changing within temperature.

This work was financially supported by the Polish State Committee for Scientific Research (134/E-365/SPUB-EUREKA/T-09/DZ024/98).

PROTON CONDUCTING POLYMER GELS CONTAINING HETEROPOLYACIDS

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Proton conducting polymer gels based on poly(vinylidene fluoride) (PVdF) and poly(methyl methacrylate) matrices doped with heteropolyacids ($\text{H}_3\text{Mo}_{12}\text{O}_{40}\text{P} \cdot x\text{H}_2\text{O}$ – (PMA); $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ – (PWA); $\text{H}_4\text{O}_{40}\text{SiW}_{12} \cdot x\text{H}_2\text{O}$ (PSA)) were synthesized and characterized by impedance spectroscopy, cyclic voltammetry, FT-IR and DSC experiments. As solvents propylene carbonate (PC) or dimethyl formamide (DMF) were used. The results of these studies are compared with previous studies on analogous systems doped with H_3PO_4 . It has been found that electrolytes doped with heteropolyacids exhibit much higher ambient temperature conductivities (exceeding 10^{-3} S/cm) than systems doped with H_3PO_4 . Colorless, chemically stable over long period of time electrolytes were obtained using PSA as the additive.

From the viewpoint of the possible application of these gel electrolytes in electrochromic devices their electrochemical stability was studied by means of voltammetric technique. Stability window of basic organic solvents (DMF, PC) used for gel synthesis has been determined on a platinum working electrode. It has also been found that monomers used for synthesis of these electrolytes do not react at the platinum electrode in the stability window potential range. This was followed by the electrochemical investigations using WO_3 working electrode performed in the absence of organic monomer molecules in order to eliminate their possible adsorption. The reproducibility of WO_3 reduction-oxidation reaction in acid solution in DMF or PC was analyzed and compared with available data on aqueous and non-aqueous lithium electrolytes. It has been found that this stability window weekly depends on the type of proton donor molecule used.

Acknowledgments:

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NOVEL "POLYMER IN SALT" TYPE ELECTROLYTES

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An important problem related to the application of lithium polymeric electrolytes in energy storage and conversion devices is connected with the low cationic transport number in these systems. It is widely acknowledged that the anions are dominant charge carriers in polymeric electrolytes and the cation transport number is usually close to ~ 0.1 . The low cationic transport number results in the formation of "anionic clouds" close to the lithium anode-electrolyte interface which blocks the diffusion of Li^+ cations to and from the electrode which is a severe limitation of the lithium cell performance.

Taking this into consideration there is an interest in the preparation of polymer solid electrolytes with the high cation transport number. One possibility is the synthesis of so-called "polymer in salt" system in which high amount of salt is mixed with a small fraction of polymer which permits mechanical integrity of electrolytes. In these systems special emphasize is put on the presence of the traces of low molecular weight compounds which might be residuals of the solvent used in the preparation procedure or traces of the unreacted liquid monomer. These low molecular weight liquids might considerably increase anionic transport number as well as affected the electrolyte-electrode interface. Therefore in the present work in situ polymerization of the solid monomers performed in the presence of the salt is used to avoid the presence of even traces of low molecular weight liquids. The monomers are melt which is followed by thermal polymerization performed in the melting phase in the presence of plasticizing salts such as lithium sulfonimides. Ambient temperature conductivities in the range of 10^{-5} - 10^{-4} S/cm are reported depending on the polymerization procedure and type of monomer used. The results are compared with data obtained for electrolytes based on the same monomers which are polymerized via free-radical polymerization performed in the solution of lithium salt in highly polar organic solvents.

Acknowledgments: This work was financially supported by the President of the Warsaw University of Technology in the frame of the 504/G/0006 Research Program.

POLYMER SOLID ELECTROLYTES WITH
ENHANCED CATION TRANSPORT NUMBER

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Poland*

The present work deals with the application of calixarenes in the synthesis of novel polyether based electrolytes leading to an enhancement in the cationic transport number of the system studied over values reached for pure polyether - alkali metal salt type electrolytes. The synthesis of p-tert-butoxycalix[4]arene derivatives capable of selective complexation of halogenic anions is presented and their complexation abilities are discussed. The grafting of the calixarene with the polyether chain is proposed and the synthetic procedure will be described in details. Preliminary characterization of physical-chemical properties of the synthesized electrolytes is described.

Acknowledgments:

This work was financially supported by the President of the Warsaw University of Technology in the frame of the 503/G/0006 Research Program.

A COMPARISON OF IONIC CONDUCTIVITY, THERMAL BEHAVIOUR AND MORPHOLOGY IN TWO POLYETHERS-LiI-LiAl₅O₈ COMPOSITE POLYMER ELECTROLYTES.

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The effect of LiAl₅O₈ addition on the properties of electrolytes prepared with PEO (Mw = 1x10⁶) and a triblock copolymer [poly(propylene glycol – ethylene glycol – propylene glycol)] with Mw = 2000, has been studied. The aluminate ceramic powder was prepared by coprecipitation and calcined at 1150 °C. The main goal of the present investigation was to compare the two classes of composite electrolytes with a polyether/LiI composition fixed at n = molar ratio of [O]/[Li] = 20. The LiAl₅O₈ powder was dispersed by ultrason on the electrolyte matrix in a range of concentrations up to 20 wt%. DSC curves indicated that all materials are semicrystalline and the triblock composites show a smaller T_g (-28°C at 20 wt% of ceramic) than the PEO electrolytes (-16°C to 20 wt% of ceramic). Thermomechanical analysis were performed using penetration mode and the composite electrolytes exhibited a significant increase in mechanical stability. Ionic conductivity of both systems (PEO and triblock – LiI – LiAl₅O₈) presented values of 5x10⁻⁴ S.cm⁻¹ at 80°C. The triblock composite shows a conductivity one order of magnitude higher than the PEO material near room temperature as a consequence of its decrease in crystallinity after a first heating. This result point out the interest in developing composites based on a triblock polyether.

MICRO-RAMAN STUDY OF POLYMER ELECTROLYTES NEAR PHASE SEGREGATION COMPOSITIONS

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Near salt separation concentrations of PEG/MClO₄ (M = Li and Na) electrolytes have been studied by micro-Raman spectroscopy at room temperature. Three poly(ethylene glycol) (PEG) with molecular weights 200, 400 and 6000 were used as matrices for lithium and sodium perchlorates between $n = [O]/[M] = 30$ to 2. The analysis of the Raman band associated with the ν_1 symmetric stretching mode of ClO₄ anions shows the presence of "free ions", contact ion pairs, higher aggregates and salt micro-separation, whose occurrence is dependent on the salt concentration, chain lengths and cation type. Evidences about the polymer-cation complexation have been obtained from the analysis of the cation-induced mode near 860 cm⁻¹. The dependence of the results on the molecular weight of the polymer host is ascribed to the interplay between the complexations by the oxygen ether and the hydroxyl end-groups.

NEW SOLID IONIC CONDUCTOR BASED ON
POLY(ETHYLENE OXIDE) AND SODIUM TRIFLUOROACETATE

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Solid polymer electrolytes consisting of poly(ethylene oxide) (PEO) and sodium trifluoroacetate (CF_3COONa) with various salt mass fractions ($x \leq 0.52$) have been prepared by solvent casting method. Temperature and concentration dependent impedance studies of the cells M/electrolyte/M (M= stainless steel electrodes), as well as the conductivity behavior of the electrolyte suggest the existence of a complex in the blend. This is confirmed by differential scanning calorimetry (DSC), showing that the melting point of the complex is at 410 K. The conductivity (σ) of the electrolyte is very sensitive to temperature (T) and salt mass fraction (x) in the blend: samples with low salt concentration shows a linear dependence of $\ln \sigma$ with $(1/T)$ below 343 K (the eutectic melting temperature of PEO + complex), with an activation energy of 0.1 ± 0.05 eV, and an almost flat variation above this temperature. The sample with concentration $x = 0.306$ shows only one activated process in the whole temperature range ($T < 410$ K). Typically, blends with the highest salt concentrations exhibit an anhydrous conductivity of $10^{-4} \text{ S cm}^{-1}$ at 303 K and 10^{-3} Scm^{-1} at 313 K. The results are discussed in terms of the high mobility of the Na^+ ions in the amorphous phase of the complex.

**MORE THERMAL STUDIES ON THE PVAI+H₃PO₂+H₂O
SOLID PROTON CONDUCTOR GEL**

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We synthesized solid protonic conductor gels using 31000-50000 average molecular weight and 98-99 % hydrolyzed poly (vinyl alcohol) (PVAI), hypophosphorous acid (H₃PO₂) and water as prime chemicals; seven OH/P concentrations (0.02, 0.05, 0.075, 0.1, 0.15, 0.25 and 0.5) were prepared. In earlier papers [1-3] we have showed that this complex is suitable for technological applications. Related to this system we have reported [1-3] about sample preparation and ionic conductivity, fuel cell, X-ray, differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements. In this paper we will report about other thermal studies performed by using the ac calorimetry method, which is more sensitive than the DSC method.

The DSC thermograms showed a well-resolved step anomaly at about 162 K, associated to a glass transition, for the three highest acid concentrations samples (OH/P: 0.02, 0.05, 0.075), and not glass transition was detected for the other concentrations; however, the ac method showed this transition for all OH/P ratios, excepting OH/P = 0.5 (the lowest acid concentration sample), in the 162-175 K temperature range. These results indicate that: 1) the samples have a certain grade of amorphousness and 2) the effect of increasing the acid concentration on T_g was negligible, which might be due to the presence of a polymeric phase with constant composition PVAI/H₃PO₂/H₂O and a separate second phase with composition H₃PO₂/H₂O.

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ION TRANSPORT PROPERTIES IN HIGH MOLECULAR WEIGHT POLYETHER COMB POLYMERS

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Ion transport in polyether-based polymer electrolytes is considered to be cooperative with local segmental motion of the polymers. Our working concept of the molecular design to achieve highly conducting polymer electrolytes is that fast molecular motion of short and flexible ether side chains in the matrix polymers would contribute to fast ion transport. In this study, high molecular weight polyether comb polymers, poly[ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidyl ether] P(EO/MEEGE) [1,2], have been used as matrixes of polymer electrolytes, and the effects of the structures of complexed lithium salts and the addition of inorganic fillers on the ion transport properties have been explored in detail. The high molecular weight ($> 10^6$) polymers allowed to give self-standing and elastic polymer electrolyte films without chemically cross-linked structures at room temperature. Lithium salts of polymeric imide anions, poly(2-oxo-1-difluoroethylene sulfonylimide lithium) (LiPEI) and poly(5-oxo-3-oxy-4-trifluoromethyl-1,2,4-pentafluoropentylene sulfonylimide lithium) (LiPPI), as well as that of monomeric imide anion, lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), were complexed with P(EO/MEEGE), and the ion transport properties were compared in terms of ionic conductivity and transference number. The change in the transport properties with the addition of acidic-oxide nano-fillers is also presented.

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ACID + ORGANIC BASE DOPED POLYMERS FOR FUEL CELL ELECTROLYTES

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New membranes for polymer electrolyte fuel cells (PEMFC) that remain conductive at temperatures above 100°C are desired if methanol or carbon monoxide containing hydrogen from reformed hydrocarbons are to be used as fuels. As well as faster reaction kinetics, and hence higher current densities achievable at elevated temperature, the faster removal of product water from the cathode may enable a simplification of water management within the fuel cell. Phosphoric acid doped polybenzimidazole (PBI) has shown promise for this application although phosphoric acid has the drawback of having low oxygen solubility with a resultant decrease in fuel cell performance. Recently, solutions of imidazole and an acid have shown high proton conductivities in the absence of water[1] making this type of proton conductor attractive for use in PEMFC membranes operating at elevated temperature.

We have identified a number of related liquid proton-conducting electrolytes, based on organic molten salts and/or imidazole compounds, as candidates for impregnation into polymer membranes. Polymer membranes having hydrophilic groups (PBI or Nafion) or a high degree of porosity to accommodate the electrolyte (porous polytetrafluoroethylene) were found to be suitable. These polymers also have high temperature stability and are resistant to attack by acids and the oxidising and reducing atmospheres found in operating fuel cells. Figure 1. shows the conductivity data for a Nafion membrane impregnated with an imidazole + acid electrolyte. As can be seen in Figure 1. the conductivity continued to increase at temperatures beyond 100 °C indicating that these proton conductors show potential as polymer fuel cell electrolytes.

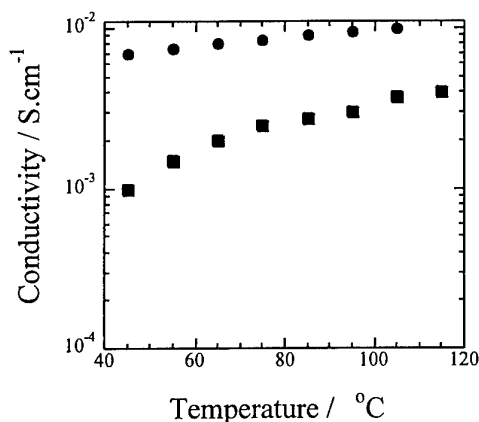


Figure 1. Conductivity data (circles) of liquid electrolyte (1,2-dimethyl Imidazole + trifluoroacetic acid) and (squares) the same liquid electrolyte impregnated into Nafion.

IONIC CONDUCTIVITY AND INTERFACIAL STUDIES OF THIN
FILM POLYMER ELECTROLYTE (PEO:LiF₆PO₄) / Li₂ O.V₂O₅ ELECTRODE

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This paper reports the preparation and characterization of evaporated polymer electrolyte films obtained from poly (ethylene oxide) (PEO) and LiF₆PO₄. Thin polymer electrolyte films are formed by evaporating a suitable mixture of PEO and LiF₆PO₄. The films are found to exhibit a considerably high ionic conductivity of about 1.7×10^{-4} S/cm at room temperature. The evaporated films are partially composed of structure similar to that of the molten state of PEO, the melting point being diffuse in the range -20 and ~50°C. The conductivity enhancement room temperature in the evaporated films can probably be attributed to the molten state structure regions. Differential scanning calorimetric (DSC) and electrical conductivity measurements are reported. The interfacial impedance of the evaporated films with intercalated electrode Li₂O.V₂O₅ is also reported. The surface layer resistance of P(EO): LiF₆PO₄ /Li₂ O.V₂O₅ films are found to be about 9.7×10^{-3} ohms at room temperature.

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ANOMOLOUS DIFFUSION IN IMIDAZOLIUM IODIDE SALTS

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A series of molten salts based on 1,3-methylalkylimidazolium iodide exhibit some excellent properties in the molten state making them attractive materials for electrolytic applications [1]. However, an unusually high conductivity (of the order of 10^{-3}Scm^{-1}) was measured in the solid state for the methyl and ethyl salts [1], prompting an investigation of the conduction mechanism through NMR diffusion experiments. Proton diffusion coefficients were measured as a function of temperature and are representative of the cation diffusion. Analysis of diffusion below the melting points (350K) displayed some anomalous behaviour with several different diffusion processes detected. This behaviour seemed to be somewhat dependent on the thermal history of the sample. Above the melting points of these salts however, only a single diffusion process occurred. Such observations imply that the transport mechanism in the solid state is very different to that in the liquid state. Further discussion of this complex diffusion behaviour and the implications on the conductivity will be presented here.

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**LITHIUM ION CONDUCTIVITY IN
POLYOXYETHYLENE / POLYETHYLENIMINE BLENDS.**

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The proclivity of polyoxyethylene(PEO) to crystallize is a great obstacle to achieving high lithium ion conductivity near room temperature in these most extensively studied polymer electrolyte systems. Quite similar situations exist for polyethylenimine(PEI)-lithium salt systems, which we have been studying[1]. In the hope that mixing PEO with PEI might hinder each other's crystallization and give rise to more viable matrices, we dissolved LiClO_4 in PEO/PEI (8/2, 5/5, and 2/8 by repeat units) blends and examined the lithium ion conductivity. The LiClO_4 contents chosen, expressed in (O+N)/Li mole ratios, were 4, 7, 10, and 15. Comparisons were made with typical PEO systems reported in the literature.

In the 8/2 blends, conductivity increased with the decrease in the salt content. Conductivities in the 8/2- and the pure PEO systems were comparable at temperatures higher than 350 K. The drastic conductivity drop, which is observed in the PEO systems below 350 K, did not occur in the 8/2 systems. The 8/2 systems consequently became 3-4 orders of magnitude more conductive than the PEO systems at room temperature. In contrast, the 5/5 systems suffered severe conductivity drop near 330 K, resembling that for the pure PEO matrices. In the 2/8 systems, the abrupt conductivity drop again disappeared. They were more conductive than the pure PEI systems. Weak temperature dependence of conductivity made their room temperature conductivity even higher than that for the pure PEO systems.

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MOLECULAR DYNAMICS SIMULATIONS OF
PEO-NaI POLYMER ELECTROLYTES

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We present the results of a detailed molecular dynamics study of poly(ethylene-oxide) (PEO) NaI polymer electrolytes. We focus on the influence of the salt on the dynamics of the polymer segments. This is done by calculating the mean square displacements of the CH₂-groups and comparing the corresponding self part of the intermediate scattering function with neutron spin-echo experiments. Three different systems are studied: pure PEO, PEO-NaI with reduced ion charges to overcome the problem of clustering, and PEO-NaI with springs between the O atoms and Na ions.

Simulations of pure PEO are in good agreement with the experimental results, indicating the validity of the PEO model. On adding NaI, a slowing down is observed in both the PEO-NaI models. However, when reduced charges are used, this effect is small compared with the experimental observations. This suggests that in this model the Na-O interaction is too weak and that O-Na-O cross-links are not formed. Adding harmonic springs between Na and O results in a better agreement with neutron spin-echo experiments.

**SYNTHESIS OF MOLTEN SALT-TYPE POLYMER BRUSH
AND EFFECT OF BRUSH STRUCTURE ON THE IONIC CONDUCTIVITY**

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Room temperature molten salts (MS) were reported to be obtained by the combination of imidazolium cation and specific anion [1]. Improvement of ionic conductivity of polymer electrolytes has been tried by using these MS [2]. However, the ionic conductivity of MS having vinyl groups decreased remarkably after polymerization [2]. PEO derivatives having both vinyl group and imidazolium cation unit were prepared expecting flexible tethering effect of PEO chains even after polymerization [3]. MS-type polymer brushes showed high ionic conductivity corresponds to that of monomers.

In this study, macromonomers having different EO unit number ($n = 2$ or 8) were prepared to analyze the effect of flexible spacer. The ionic conductivity of MS polymers increased with increasing EO unit number, reflecting the improved local motion of imidazolium salt on the chain end. On the other hand, in spite of different imidazolium cation species, the ionic conductivity and T_g of a series of macromonomers and their polymers were almost identical. Strategy of the design of MS polymer brush for higher ionic conductivity will also be mentioned.

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[2] H. Ohno and K. Ito, *Chem. Lett.*, (1998) 751-752.

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ALL SOLID-STATE SMART WINDOW OF ELECTRODEPOSITED WO_3 AND SnO_2/MO
FILM WITH POLYMER GEL ELECTROLYTE

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Intensified research efforts to develop electrochromic devices have spread worldwide in recent years. The focus of these research programs is on large area window applications. For such applications, all solid state electrochromic devices have unique advantages (such as reliability and safety) when compared to conventional liquid-based devices. Lithium-based devices have attracted increasing attention because of their environmental stability. Most lithium-based solid polymer electrolytes are a mixture of LiClO_4 and various polymers, such as polyethylene oxides (PEO). However, the conductivity of the solid polymer electrolyte on the order of 10^{-9} to 10^{-5} S/cm at room temperature is still too low for practical applications, for which a conductivity greater than 10^{-4} S/cm at room temperature is required to minimize the ohmic drop across the smart window. The identification of polymer electrolytes with conductivities of about 1 mS/cm at room temperature remained an ambitious goal. An all solid-state smart window of electrodeposited WO_3 and SnO_2/Mo film with polytrithylene glycol dimetrocrylate (PTREGD) gel electrolyte with high conductivity (1 mS/cm) at room temperature has been fabricated. The electrochromic smart window has been found to be excellent for electrochromism and memory characteristics.

PREPARATION OF ION CONDUCTIVE DNA FILMS

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Apart from the importance of DNA in the life science, DNA is quite interesting material because of rigid and rod-like polyelectrolyte. Since it is also easy to prepare DNA films¹⁾, these characteristics are applied to prepare new polymer electrolyte films with the aid of PEO derivatives.

The films prepared from aqueous solution of only DNA was brittle and hard to treat as film materials. The DNA films turned flexible after addition of PEO. Ionic conductivity was detected when salt was added to the DNA films. PEO derivatives were considered to fix electrostatically with phosphate anion residues of DNA. PEO having imidazolium cation unit on the one or both ends (PEO-EtIm) were used expecting molten salt formation. The highest ionic conductivity for DNA/PEO₇₅₀-EtIm films was 4.89×10^{-5} (S/cm) at room temperature.

DNA contains four kinds of bases. These hetero aromatic rings can be regarded as interesting components to form molten salt. Some model bases except thymine were equimolarly mixed with HBF₄ in water. The melting point of the products was considerably decreased about 50~120°C. The mixture of phosphoric acid and ethylimidazolium became highly viscous liquid with no melting point. The ionic conductivity was 5.8×10^{-5} (S/cm) at room temperature. According to their model experiments, DNA was expected to be interesting film materials having molten salt domain.

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PEO-BASED NANOCOMPOSITE POLYMER ELECTROLYTES:
AN IMPEDANCE SPECTROSCOPY STUDY

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Lithium polymer electrolytes formed by dissolving a lithium salt in poly(ethylene oxide) PEO may find useful application as separators in lithium rechargeable polymer batteries. The main drawback of solvent-free PEO-based polymer electrolytes is their high crystallinity at room temperature, which reduces the conductivity to a level too low to satisfy the requirements of batteries or other devices. In this poster we show that the addition of nanometric filler (SiO_2 , TiO_2) in $\text{P(EO)}_n\text{LiClO}_4$ polymer electrolytes induces an increase of the transport properties respect to the corresponding unfilled ceramic-free polymer electrolyte. The increase in conductivity and cation transference number was attributed to the enlargement of the total amorphous phase in the polymer matrix and also to some possible ceramic-electrolyte interactions in according to an acid-base Lewis mechanism [1,2,3].

In order to study the effect that the addition of nanometric filler has on the crystallization kinetic of P(EO)-based polymer electrolytes we have undertaken an impedance spectroscopy study on samples with and without the ceramic filler. In particular in this poster we show that the nanometric filler can perform as a solid plasticizer for PEO by kinetically inhibiting crystallization. Furthermore, our results show that the filler addition deeply influences both the electrical conductivity and the fraction of the current transported by the cations of the samples.

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- 2) R. Caminiti, F. Croce, A. Martinelli, L. Persi, F. Ronci and B. Scrosati *J. Phys. Chem.*, in press
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STUDY ON THE REDOX REACTION OF
POLY(ETHYLENE OXIDE)-DERIVATIVE MODIFIED MYOGLOBIN
ON THE ELECTRODE SURFACE IN PEO OLIGOMERS

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Myoglobin showed electron transfer reaction at electrode in PEO oligomers, only when Myoglobin was modified with PEO-derivatives. However, this electrochemical redox response is slow in PEO oligomers. In this study, we investigated the immobilization methods of PEO-Mb at the electrode in order to suppress the diffusion of the PEO-Mb and to obtain stable redox response of immobilized Mb.

PEO-Mb was immobilized on the carbon electrode by adsorption or cast methods. The redox responses of immobilized Mb were measured by cyclic voltammetry. However the electron transfer of PEO-Mb was observed, the peak current was gradually decreased with time. One of the reasons for this decrease was the gradual removal of the immobilized PEO-Mb from the electrode surface. In order to obtain stable redox reaction of Mb at the electrode, Mb was chemically bound onto the electrode surface via PEO derivative spacer. The PEO-maleic anhydride copolymer was reacted with carbon electrode surface in dichloromethane. Mb was then reacted with this copolymer fixed on the carbon electrode in an aqueous medium. Stabilization of the redox response of Mb bound to the copolymer was analyzed potentiometrically. Other PEO derivative spacers were also evaluated for better electrode response.

COMPOSITE POLYETHER ELECTROLYTES WITH LEWIS ACID TYPE ADDITIVES

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Polymer electrolytes based on low molecular weight PEG ($M_w=350$) doped with LiClO_4 (0.1-1 mol kg PEG) and containing up to 10 mass % of AlBr_3 additive were synthesized and characterized by impedance spectroscopy, cyclic voltammetry, FT-IR, DSC and rheological techniques. It has been found that addition of small amount (up to 1 mass %) of AlBr_3 increases electrolytes conductivity in comparison with pure PEG- LiClO_4 electrolytes. Room temperature conductivity as high as 3×10^{-4} S/cm were measured. For higher AlBr_3 concentrations stiffening of the polymer organic electrolyte was observed which results in a decrease in the ionic conductivity.

According to previous literature reports certain Lewis acid type additives influence the interfacial phenomena at the lithium electrode polymer electrolyte interface. We have undertook systematic studies of these phenomena in the symmetrical cell comprising two lithium electrodes separated by PEG- LiClO_4 - AlBr_3 electrolyte. The changes of overall electrode impedance as well as of the separate parameters of an equivalent electrical circuit allow us to postulate different rate of SEI (solid electrolyte interface) formation and limitation of its growth in the presence of AlBr_3 interface thus enhancing the effectiveness of lithium cells.

Acknowledgments:

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GROWTH AND CHARACTERIZATION OF LEAD-SULFIDE DEPOSITED ON GLASS SUBSTRATES

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Lead-sulfide (PbS) films have been deposited by the chemical deposition method on glass substrates. The details of the preparation method are described. The advantage of this method is that it is simple, relatively inexpensive, easily controlled and able to produce large area films. Some data about the electrical properties, the structure, composition of the films, and the thermal stability of the powder samples are also presented. The structure and the crystallite sizes were determined from X-ray diffraction studies. The films are very adherent to the substrates. The film is polycrystalline and the average crystallite size is 15nm. The surface morphology of the as-deposited and heated lead-sulfide films was studied with a scanning electron microscope. The rate of deposition and terminal thickness has been established. Hall measurements were performed at room temperature for PbS films deposited on glass substrates to determine the conduction type, the carrier density, the Hall mobility and the mean free path of the carriers.

LOCAL FREE VOLUME AND STRUCTURE OF POLYMER GEL ELECTROLYTES ON THE BASIS OF ALTERNATING COPOLYMERS

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The relationship between the structure of the polymer and the ionic conductivity has been studied for a new class of gel electrolytes on the basis of alternating copolymers, which were prepared by photopolymerization of maleic anhydride (MAN) and tetra (ethylene glycol) divinylether ((EG)₄DVE) in the presence of various oligo(ethylene glycol)_n dimethylether ((EG)_nDME) and LiCF₃SO₃ [1]. Electrochemical and mechanical properties are promising [2]. However the ionic conductivity is rather low.

Gels based on poly(MAN-alt-(EG)₄DVE) are heterogeneous materials composed of a highly crosslinked polymer network ($M_c \approx 600$ g/mol) with $T_g \approx 100^\circ\text{C}$ and of a plasticizer salt solution with $T_g \approx -70^\circ\text{C}$ as determined by means of differential scanning calorimetry and dynamic mechanical analysis. In result of a free volume study by positron annihilation lifetime spectroscopy, two hole size distributions were estimated around 0.26 nm and 0.34 nm related to the network and the liquid phase, respectively. The charge carrier transport occurs within the liquid phase of the gel as indicated by Raman spectroscopic investigations (high content of symmetrical LiO₆ complexes) and a low dependence of the self-diffusivity of charge carriers and plasticizer (measured by pulsed field gradient NMR) on the content of the polymer in the gel.

Ionic conductivity and self diffusivity of the charge carriers of these gel electrolytes are not related according to the Nernst-Einstein relationship. The relatively low positronium bubble size (considering the macroscopic surface tension of (EG)_nDME) and the observed strong dependence of the self-diffusion coefficients of plasticizer and charge carriers on the molar mass of (EG)_nDME indicate that the polymer is too dense to provide optimal mobility and distribution of the plasticizer.

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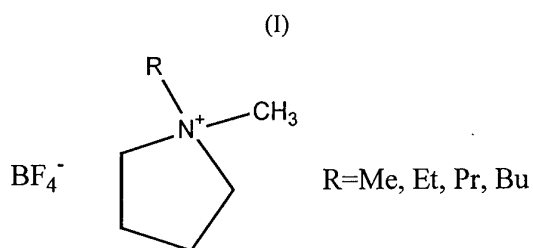
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PYRROLIDINIUM TETRAFLUOROBORATE IONIC LIQUIDS
AS POTENTIAL SALTS FOR POLYMER ELECTROLYTES

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A series of novel N-alkyl-N-methylpyrrolidinium tetrafluoroborate salts (I) have been prepared. Their physical, spectroscopic and electrochemical characteristics have been determined in order to ascertain their viability for use in polymer in salt electrolytes.



**A NMR STUDY OF POLYMER GEL ELECTROLYTES
BASED ON A POLYMER WITH GRAFTED PEO-SIDE CHAINS**

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Ion containing polymers and polymer based systems have attained a large interest as electrolytes in rechargeable lithium batteries. The combination of solid properties, flexibility and ionic conductivity provides several advantages as compared to conventional liquid electrolytes. Polymer gel electrolytes, where a polymer is dissolved in a liquid electrolyte combines the high conductivity of liquid electrolytes with fairly high mechanical stability. In PMMA based gels it has been seen that the polymer is almost inert in the gel and that this can cause a phase separation to occur. By functionalising the acrylate backbone with PEO-chains, the interactions in the gel system can be modified to be high enough to prevent phase separation, but still low enough to promote the ionic conduction. In this study we have used four polymers, differing only in the length of the PEO side chains. The backbone consists of a copolymer of two acrylates, with grafted PEO side chains. The weight fraction of PEO in all polymers are constant, while the chain length of the PEO side chains are varied (1,2,5 and 9 EO units).

Raman studies have shown that the preferred interaction changes from solvent/Li ions to polymer/Li ions when the lengths of the PEO side chains are increased. In this study we have used Li-7, C-13 and H-1 NMR to further investigate the gel systems. We have seen that the mobility of the PEO side chains is in the same order of magnitude as the mobility of the polymer backbone, while the mobility of the solvents are at least 10 times higher. This indicates that the system is dynamically inhomogeneous, even if the components in this system experience stronger interactions than the systems based on the inert polymer PMMA. The results from these measurements will be discussed in more detail here.

FREE VOLUME AND IONIC MOBILITY IN NANOCOMPOSITES OF POLYETHER
ELECTROLYTES STUDIED BY POSITRON ANNIHILATION LIFETIME SPECTROSCOPY
(PALS) AND Li-7 NMR

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In this study we report on positron annihilation lifetime spectroscopy and ⁷Li NMR measurements on an amorphous polymer based electrolyte, 1.5 mol/kg LiClO₄ containing polyether urethane (PEU). The PEU is a random copolymer of ethylene glycol and propylene oxide, crosslinked with hexamethylene diisocyanate, here referred to as 3PEG. Earlier studies of these systems have shown that the conductivity is increased when adding 10w% TiO₂ to this polymer and Raman studies have shown that the amount of ion pairs is decreased with the addition of filler, especially at higher temperatures. The increase in free ions is, however, not enough to explain the increase in conductivity. Therefore, we have conducted positron annihilation lifetime spectroscopy on a series of samples with different amount of fillers, ranging from 0 to 16 weight percent of TiO₂ in order to investigate if the fillers influence the free volume of the system. In addition, ⁷Li NMR measurements have been conducted on the same system showing a decrease in the mobility of the lithium ions, indicating a restricted mobility of the cations with addition of the filler. This latter result is in good agreement with previous Raman results indicating a loss of segmental flexibility of the polymer chain upon adding nanofillers but seemingly in contradiction to the measured conductivity.

The results will be discussed in terms of inter- and intra-chain transport mechanisms in nanocomposite polymer electrolyte systems.

CONDUCTION PROPERTIES OF LITHIUM GEL ELECTROLYTES
INVESTIGATED BY IMPEDANCE SPECTROSCOPY AND
PULSED-FIELD GRADIENT NMR WITH ELECTRIC FIELD

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Conduction properties of gel polymer electrolytes composed of lithium imide salts, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ and PVDF-HFP copolymer were investigated using the pulsed-field gradient (PFG) NMR and complex impedance techniques. The diffusion coefficients of the gel decreased with an increase in the polymer fraction in the gel. Carrier concentration exhibited a three order of magnitude variation in the fraction change in polymer from 80 wt% to 20 wt%. These results suggest that the polymer interacts with the electrolyte to affect the carrier concentration and mobility of the gel electrolytes. The interactive effect of polymer would be detected in the measurements of spin-lattice relaxation time (T_1). The deviation of the symmetric curve of the temperature dependence of T_1 could be divided into two components, one was consistent with the component of solution and independent of the polymer fraction, and the other depended on the polymer fraction in the gel. Furthermore, the electric potential was applied to the cell for diffusion measurement in the PFG-NMR in order to select the migration of ions to estimate the ionic mobility. Dissociation degree of the salt in the gel also discussed from the analyses of the NMR results.

**EFFECT OF MOISTURE ON MOBILITY IN
POLYACRYLONITRILE-LITHIUM TRIFLATE ELECTROLYTES**

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Polymer in salt electrolytes (PISE) are systems which exhibit significant ionic conductivity below their glass transition temperatures, in contrast to conventional polymer electrolytes (SPEs). The conductivity of PISE, in particular the poly(acrylonitrile)-lithium triflate electrolyte system (PAN/LiTF) has previously been found to increase by nearly four orders of magnitude upon uptake of a few wt.% of moisture from the atmosphere. In comparison, the conductivity of conventional SPEs increases by around one order of magnitude upon exposure to atmospheric moisture. This paper investigates the mechanism by which moisture produces such a substantial increase in conductivity in PISE samples.

Samples were exposed to deuterium oxide, and the deuterium NMR spectra measured to find out about the mobility of the water molecules in the samples. Lithium NMR spectra were also measured, to study the changes in lithium mobility caused by exposure to moisture. DSC measurements were performed, to determine the effect of moisture on the glass transition temperature of the PAN in the samples. Samples with around 1 wt.% of D₂O added showed no deuterium NMR signal, indicating that the D₂O was in an immobile state. At slightly higher D₂O concentrations, a narrow peak with a broad base was observed, indicating that some of the D₂O was now in a mobile state. The lithium spectra for sample with around 1% D₂O added indicated the presence of both mobile and immobile lithium in the samples, while at higher D₂O concentrations, only a narrow lithium peak was observed. The glass transition temperature of the PAN decreased with exposure to moisture, although it was still above room temperature. We propose a mechanism where the moisture is coordinated to the lithium ions, reducing the interactions between lithium ions and the PAN, and hence increasing conductivity and decreasing glass transition temperature. The large increase in conductivity with small amounts of moisture may be indicative of domains of moist salt percolating through the sample and providing highly conductive pathways.

LITHIUM ION CONDUCTION IN CERAMIC-POLYMER COMPOSITES

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Composites of lithium aluminium titanium phosphate and a polyether/lithium triflate electrolyte have been prepared. The impedance spectra for these composites contain multiple flattened semicircles. Several different equivalent circuits fit the impedance data, meaning that conclusions about the conduction mechanism in the composites cannot be made on the basis of the impedance spectra. However, the total conductivity values obtained are independent of the equivalent circuit used. At room temperature, only composites containing 36 vol. % and 47 vol. % ceramic were more conductive than the base polymer electrolyte, whilst at 80°C all compositions were more conductive than the base polymer. The conductivity values for the 36 vol. % and 47 vol. % samples were 2×10^{-5} S/cm at room temperature (where the base polymer has a conductivity of 1×10^{-5} S/cm) and 7×10^{-4} S/cm at 80°C, compared to 2×10^{-4} S/cm for the unfilled polymer. These changes in conductivity behaviour with temperature are believed to be the result of poor adhesion at the ceramic-polymer interface at lower temperatures. Evidence for this hypothesis will be presented, along with the results of some of the attempts to improve interfacial adhesion and hence conductivity.

ISPE7

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